The Properties of
GLASS

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie, Moissan's Traité de Chimie Minérale Générale, Friend's and Mellor's Textbooks of Inorganic Chemistry and Heilbron's Dictionary of Organic Compounds, it often takes a great deal of time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

PREFACE

When work was begun on this monograph in 1924, most of our knowledge of the properties of glass was due to the work of Schott and his collaborators. That work, carried on in the last two decades of the nineteenth century, dealt with glasses containing too many components and covering too small a range in composition to permit the calculation of the specific effects of the various components. It seemed desirable to make measurements with systems of few components over a large range in composition to secure more systematic knowledge; and such a research was started in collaboration with my colleague Dr. H. E. Merwin. Furthermore, at that time there was no information as to the phase equilibrium relationships in glass-forming systems. A study of them was started in collaboration with my colleague Dr. N. L. Bowen. Partly because of these studies, the results of which are included herein, and partly because of other duties, the publication of this monograph has been delayed. In the meantime, many other studies of the properties of glass have been published; of the 781 literature references, 478 of them are to work published since 1920, and 399 to work published since 1924. Thus our knowledge of the properties of glass today is far more accurate and complete than when this book was started, a result which is due not only to the interest of academic workers, but also to an awakened realization by the glass industry that the soundest foundation for a strong industry is the understanding of its fundamental scientific principles.

The information in the literature concerning the properties of glass is of widely differing accuracy and reliability, and I have indicated my judgment whenever such indication seemed desirable, and the necessary experimental details were available. I have tried to include all measurements on glasses of known composition, and throughout the emphasis has been placed on the physical properties as functions of composition.

It is a pleasure to acknowledge the advice and assistance in the preparation of this book of my colleagues: Dr. J. C. Hostetter, Vice-President, The Hartford-Empire Company, Hartford, Conn., formerly of this Laboratory and later in charge of development and research at The Corning Glass Works, Corning, N. Y.; Dr. J. T. Littleton, Chief Physicist, The Corning Glass Works; and Dr. H. E. Merwin, of this Laboratory.

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Chapter I

The History and Definition of Glass

The History of Glass

Glass has been used by man from the earliest times of which we have archeological record. Objects shaped by hand from a natural glass by primitive people have been found in widely separated localities. The glasses found in nature represent molten rock masses which were extruded and cooled so quickly that they did not have time to become transformed into the usual aggregate of crystalline minerals. The commonest of these natural glasses, obsidian, is usually translucent and blackish in color, but it is sometimes red, brown or greenish, and some varieties are transparent. It is easily broken into sharp, often elongated pieces, which lend themselves readily to the fashioning of arrowheads, spear-heads and knives; and its use for such purposes by people of Stone Age culture was widespread. In more advanced cultures, obsidian was valued also for ceremonial purposes and for jewelry; and some of the objects made from it show a high quality of handicraft.

Worked objects of obsidian have been found almost everywhere the mineral occurs, in Italy, Greece, Czechoslovakia, Hungary, and Asia Minor; and obsidian seems to have been an article of commerce as early as the Bronze Age. It was used extensively throughout the Americas. The obsidian[1] of Yellowstone Park was well known to the Indians, and was traded from tribe to tribe, often far from its place of origin. An extensive collection of obsidian tools found in a burial mound near Chillicothe, Ohio, and now in the Field Museum of Natural History, in Chicago, is considered to be made of obsidian from Mexico. Obsidian blades have been found in Patagonia,[2] and obsidian mirrors in Ecuador.[3] Hardly an occupied site in all Mexico or Central America can be found that does not furnish examples of obsidian.[4] The flake knife, which is found in great numbers in the Valley of Mexico, is the simplest and most universal of the flaked forms. They were not made at the quarry, as the edges of the blades were so delicate that transportation would have subjected them to injury; therefore the selected nuclei were carried away, and the knives made wherever they were required. Tylor[5]

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[1] The compositions of some obsidians and other natural glasses are given in Table III. 1.

[2] Outes, F. F., "La Edad de la Piedra en Patagonia"; Anal. Museo nac. de Buenos Aires, 5, 203 (1905).

[3] Saville, M. H., "Antiquities of Manabi"; Irving Press, New York, 1907.

[4] Holmes, W. H., *Am. Anthropologist*, 2, 405 (1900).

[5] Tylor, E. B., "Anhuac," Longmans, Green, Longmans and Roberts, London, 1861.

gave the following free translation from Torquemada[6] of a description of making the flake knives:

> "One of these Indian workmen sits upon the ground, and takes a piece of this black stone, which is like jet, and hard as flint, and is a stone which might be called precious, more beautiful and brilliant than alabaster or jasper, so much so that of it are made tablets and mirrors. The piece they take is about eight inches long or rather more, and as thick as a man's leg, or rather less, and cylindrical; they have a stick as large as the shaft of a lance, and three cubits or rather more in length; and at the end of it they fasten firmly another piece of wood, eight inches long, to give more weight to this part; then, pressing their naked feet together, they hold the stone as with a pair of pincers, or the vice of a carpenter's bench. They take the stick, which is cut off smooth at the end, in both hands, and set it well home against the edge of the front of the stone, which also is cut smooth in that part; and then they press it against their breast, and with the force of the pressure there flies off a knife, with its point, and edge on each side, as neatly as if one were to make them of a turnip with a sharp knife, or of iron in the fire. . . . They come out of the same shape as our barber's lancets, except that they have a rib up the middle, and have a slight graceful curve toward the point."

These obsidian blades and razors were the most efficient tools for the uses to which knives and scissors are put until well into the Age of Iron.[7] Obsidian mirrors were of widespread use, and even ceremonial masks were made from this hard material. The commonest use of natural glass by primitive people was for arrow-heads and spear-heads; and beautiful examples are to be seen in many collections. The fashioning of glass into arrow-heads and similar objects is not a lost art, but has been taken up as a hobby by several people, who have found that ordinary bottle glass is easier to work than obsidian. Arrow-heads and spear-heads thus made from ordinary glass are to be seen in the National Museum in Washington.

The Beginnings of Glass Manufacture

When glass was first made artificially is not known, but it must have been early in the cultural history of mankind. Once the discovery of fire-making had made accessible the regions of high temperature, the beginning and development of the arts based on fire followed naturally. It has been assumed that the discovery of glass came after, and was a consequence of, the development of metallurgy; but it appears

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[6] Torquemada, "Monarquia Indiana," lib. xvii, cap. i. See a correction of Tylor's translation, *Compt. rend.*, p. 47 (1926). Quoted also in Evans, Sir J., "Ancient Stone Implements, Weapons and Ornaments of Great Britain"; D. Appleton and Co., New York, 1872.

[7] MacCurdy, G. G., *Am. Anthropologist,* **2,** 417 (1900).

more probable that both metallurgy and glass-making were consequent upon the development of the potter's art. The firing of crude pottery was the first step in the development of the arts based on fire, and from this the development of glaze and thence of glass was a logical and probable step. It may be, however, that the discovery of glass was an independent occurrence. There is a great difference between a glaze and a glass, and the development of one from the other is little, if any, more probable than that each represented independent discovery. The similarity arises of necessity from the chemical properties of the material; the differences are more manifest to the non-technical observer.

Possibly the production of glass owes its beginning to accident. An illustration of such a possibility is the glass, described by Velain,[8] formed by the burning of grain and the fusion of the ash, as the result of fire caused by lightning. Such occurrences are not uncommon, and Velain said that the masses of glass found in the ash were called "lightning stones" (pierres de foudre) by the French peasants, who believed them to be the cause of the fire. Another illustration is in the following account of the origin of glass manufacture, as related by Pliny:[9]

> "In Syria there is a region known as Phoenice, adjoining to Judaea, and enclosing, between the lower ridges of Mount Carmalus, a marshy district known by the name of Cendebia. In this district, it is supposed, rises the river Belus, which, after a course of five miles, empties itself into the sea near the colony of Ptolemaïs. The tide of this river is sluggish, and the water unwholesome to drink, but held sacred for the observance of certain religious ceremonials. Full of slimy deposits, and very deep, it is only at the reflux of the tide that the river discloses its sands; which, agitated by the waves, separate themselves from their impurities and so become cleansed. It is generally thought that it is the acridity of the sea-water that has this purgative effect upon the sand, and that without this action no use could be made of it. The shore upon which this sand is gathered is not more than half a mile in extent; and yet, for many ages, this was the only spot that afforded the material for making glass.
>
> "The story is, that a ship, laden with nitre, being moored upon this spot, the merchants, while preparing their repast upon the sea-shore, finding no stones at hand for supporting their cauldrons, employed for the purpose some lumps of nitre which they had taken from the vessel. Upon its being subjected to the action of the fire, in combination with the sand of the sea-shore, they beheld transparent streams flowing forth of a liquid hitherto unknown: this, it is said, was the origin of glass."

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[8] Velain, Ch., *Bull. franc. Soc. mineral.*, 1, 113 (1878). For composition see Table III. 1.

[9] "The Natural History of Pliny"; 6, 379, trans. by Bostock, J., and Riley, H. T.; Henry G. Bohn, London, 1857.

The story is a plausible one. It has been doubted if sufficient heat could be developed by an open fire as described, but these doubts are not justified. Monroe[10] found that a wood fire kept burning two hours in the open air developed a temperature of 1200° C. (2200° F.). This temperature would be sufficient to melt not only a soda-silica glass but also a soft soda-lime-silica glass. The lowest-melting eutectic of soda (Na_2O) and silica (SiO_2) is at 793° C., and of soda, lime and silica 725° C. At these low temperatures a long time would be required to produce a clear glass, because of the great viscosity of the melt; but that glass could be formed at the higher temperature shown to be available by Monroe[10] there can be no doubt. The discovery of glass manufacture could have been made in the manner related by Pliny; but the dating of the oldest piece of glass indicates that the discovery took place hundreds of years before the time of the Phoenician traders.

The Glass of Antiquity

Where glass manufacture had its beginning is an open question. The oldest piece of glass bearing a date is a large ball-bead with the cartouche of Amenhotep (1551-1527 B.C.), now in the Ashmolean Museum, Oxford. Glass made in Egypt at about this period, the Eighteenth Dynasty, is plentiful; but earlier glass has been found whose dating is unquestionable, and still other pieces concerning the dating of which there is some difference of opinion.

Much of our knowledge of ancient glass we owe to Sir W. M. Flinders Petrie, who says:[11]

> "The earliest glaze known is that on stone beads of the Badarian age in Egypt, about 12,000 B.C. This is green. That civilization was intrusive, probably from Asia. Green glaze was applied to powdered quartz basis for making small figures about 9000 B.C., and was ever after so common in moulded beads that it was certainly of Egyptian manufacture.
>
> "The oldest pure glass is a moulded amulet of deep lapis lazuli color, of about 7000 B.C. Fragments of green opaque glass inlay appear in the First Dynasty about 5000 B.C. Striped black and white glass amulets came in the Eleventh Dynasty, about 3800 B.C. An elaborate fused glass mosaic of a calf is in jewelry of 3300 B.C. from Dahshur. Blue translucent beads appear about 1570 B.C. All of these occurrences of dateable glass in Egypt were probably due to importation from Asia." In another place he says:[12]
>
> ". . . not a single piece of glass was made in Egypt prior to about 1500 B.C. . . . There was certainly no evidence as yet as to the pro-

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[10] Monroe, W. L., "Window Glass in the Making," 21, American Window Glass Co., Pittsburgh, Pa., 1926.

[11] Petrie, Sir W. M. Flinders, *Trans. Newcomen Society*, **5**, 72 (1924-25).

[12] Petrie, Sir W. M. Flinders, *J. Soc. Glass Tech.*, **10**, 229 (1926).

duction of glass in Egypt until one came down to the period 1500 B.C., about which time one also came across sculptural records bearing representations of Syrian workmen being brought into Egypt, carrying with them the vases of metal or of glass which they had produced. There was no question that the Syrians were far ahead of the Egyptians up to this period in the matter of art and industry, and when one remembers that examples of glass had been found in Syria—in the Euphrates region—which could be definitely dated back to 2500 B.C., one had little difficulty in attributing to the Syrians the glasswares which were imported into Egypt prior to 1500 B.C."

Lucas,[13] however, says:

> "At what period glass was first produced is uncertain, and there is little doubt that it was made exceptionally and in small amount before it came into general use, and when occasional early specimens are found in Egypt there is no need to assume that they are of foreign origin and have been imported."

Lucas gives evidence that many of the specimens considered to be glass of early origin are not glass at all. For example, the bracelet of the First Dynasty, found at Abydos,[14] is turquoise. The mosaic of the Twelfth Dynasty from Dahshur,[15] which is a small pendant with the figure of an ox, is natural stone, in part lapis lazuli, in part rock crystal. The small blue Hathor head [16] in the University College Museum, London, and the greenish glass bead in the Berlin Museum,[17] both found by Flinders Petrie, are undoubtedly glass; but Lucas implied doubts as to their dating to the First Dynasty. However, there is no doubt as to the dating of the "rich blue glass beads" from Deir el Bahri,[18] found in the coffin of little Maït, a child queen of King Mentuhotpe (2196-2172 B.C.). Whether they represent native manufacture or an importation is an open question, but they may be the oldest glass of undisputed date found in Egypt.

Some evidence indicates that we must look to Asia Minor, probably in Mesopotamia, for the beginnings of glass manufacture. Glass beads were plentiful in the excavation of a cemetery of the Third Dynasty of Ur (2450 B.C.), and Petrie considers that there may have been centers of glass-making in this region long before its production in Egypt. Frankfort [19] found a cylinder of light blue glass, of excellent quality, at Tell Asmar, northwest of Baghdad. "Our cylinder dates, at the

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[13] Lucas, A., "Ancient Egyptian Materials"; Longmans Green and Co., New York; Edwin Arnold, London, 1926.

[14] Vernier, E., "Bijoux et Ortvreries"; Cat. Gen. du Musée du Caire, 1907.

[15] Newberry, P. E., *J. Egypt. Arch.*, **6**, (1920).

[16] Petrie, Sir W. M. Flinders, "Prehistoric Egypt"; 1920.

[17] Neumann, B., and Kotyga, G., *Z. angew. Chem.*, **38**, 776-80, 857-64 (1925).

[18] Winlock, H. E., "Bull. Met. Museum of Art," New York, Part 2, p. 52 (1921).

[19] Frankfort, H., "Iraq Excavations of the Oriental Institute, 1932-33"; 55, Univ. of Chicago Press, 1934.

latest, to the dynasty of Gutram, and more probably to the dynasty of Akkad," probably 2600-2700 B.C. The glass had a density of 2.463, a refractive index of about 1.515; and it appeared surprisingly free from striae or inclusions.

Whether or not the manufacture of glass was continuous in this region is not known. The famous Sargon vase, inscribed with the name of the Assyrian king Sargon II (722-705 B.C.), which was found in the ruins of Nineveh and now is in the British Museum, is considered[20] to be of Egyptian origin. It was made of a translucent greenish glass, and was evidently built up on a core, according to the technique prevalent at the time. The explorations of Thompson[21] at Nineveh gave much information of the state of the art at the time of Assurbanipal (668-626 B.C.), and his translation of certain cuneiform tablets, which appear to be factory records, is of great interest. They give not only the Assyrian names for various kinds of glass, but also directions and formulas for their manufacture. The following excerpt shows the style of this ancient treatise:

> "When thou settest out the [ground] plan of a furnace for 'minerals,' thou shalt seek out a favourable day in a fortunate month, and thou shalt set out the [ground] plan of the furnace, while they are making the furnace, thou shalt watch [them], and shalt work thyself [?] [in the house of the furnace]: thou shalt bring in embryos* [born before their time] . . .: Another [?], a stranger, shall not enter, nor shall one that is unclean tread before them; thou shalt offer the due libations before them: the day when thou puttest down the 'mineral' into the furnace thou shalt make a sacrifice before the embryos: thou shalt set a censer of pine-incense, thou shalt pour kurunnu-bber before them.
>
> "Thou shalt kindle a fire underneath the furnace and shalt put down the 'mineral' into the furnace. The men whom thou shalt bring to be over the furnace shall cleanse themselves, and [then] thou shalt set them to be over the furnace.
>
> "The wood which thou shalt burn underneath the furnace shall be styrax, thick decorticated billets which have not lain [exposed] in bundles, [but] have been kept in leather coverings, cut in the month of Ab.** This wood shall go underneath thy furnace."
>
> Translator's Notes: *"*This use of foetus or embryos in the preparation of the furnace is a question for the anthropologist rather than the chemist. It may be mentioned, however, that Frazer* (Immortality, 2, *49, note) says abortions appear to be regarded as most*

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[20] Kisa, A., "Das Glas im Alterthum"; 1, 102, K. W. Hiersemann, Leipzig, 1908.

[21] Thompson, R. C., "On the Chemistry of the Ancient Assyrians," Luzac and Co., London, 1925. A page of the original text and a translation of a portion relating to the details of glass-making are reproduced by Marshall, A. E., *Bull. Am. Ceram. Soc.*, 7, 5 (1928), and by Morey, G. W., *Art and Archeology*, 28, 199 (1929).

> *malignant. . . . Clearly the Assyrian idea is that the spirits of incomplete beings must be propitiated, on the grounds that they would have some mysterious influence over incomplete substances,* i. e., *the glass which is in progress of being made."*
>
> **"*The glass-maker is here advised to use wood which will give the maximum of heat; . . . it must have been cut in Ab, the hottest and driest month of the year."*

In Ptolemaic and Roman times, there was a well-established glass industry not only in Mesopotamia but also in Tyre, Sidon, Palestine and Syria. It is not known whether this was the descendant of the native industry or the result of the expansion of the Alexandrian glass industry.

The presence of a stable domestic glass industry in Egypt at the beginning of the Eighteenth Dynasty is shown by the remains of glass-works of that period,[22] which are still to be seen. Hilprecht [23] considered that the end of this dynasty corresponded to the best period of Egyptian art, especially in glass; and the composition of the glass of this period gave a product more durable than that of later periods, also requiring more technical competence in its manufacture. From this time until the first part of the Christian Era, Egypt remained the chief center of glass manufacture; and its glassware was distributed throughout the world.[24] The industry became centralized at Alexandria, from which place, under the stimulus of the Ptolemaic revival, it was carried to Syria, Palestine, Greece, and Italy.

The first mention of glass in India was in the time of the Singalese kings, doubtless as the result of the contacts with that region established by Alexander. Until recently [25] it was believed that the first glass in China was imported from Alexandria, and that glass-making was introduced subsequent to that time. Recent work, however, has shown [26] that glass, probably of native manufacture, was used for decorative purposes in China in 550 B.C. Both barium oxide and lead oxide have been found [27] in these ancient Chinese glasses, which range in density from 3.25 to 5.25. Barium oxide is not known otherwise as a constituent of ancient glasses; and later Chinese glasses, of T'ang times, were of the common soda-lime-silica and soda-lime-lead oxide-silica types.

The earliest glass-making differed in its chief purpose from glass-

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[22] Newberry, P. E., *J. Egypt. Arch.*, **6**, (1920).

[23] Hilprecht, H. V., "Explorations in Bible Lands"; Philadelphia, 1903.

[24] The blue glass bead found at Aghnaskeagh, County Louth, Ireland, and dated to about 500 B.C. [O'Riorda'in, S. P., *Discovery*, **16**, 100 (1935)] may be of Egyptian origin.

[25] Sarton, G., "Introduction to the History of Science," **1**, (Publication No. 376, Carnegie Institution of Washington); Williams and Wilkins, Baltimore, 1927.

[26] Sarton, G., *Isis*, **25**, 73 (1936). White, W. C., "Tombs of Old Lo-yang"; Shanghai. Kelly and Walsh, 1934.

[27] Beck, H. C., and Seligman, C. G., *Nature*, **133**, 982 (1934). Seligman, C. G., Ritchie, P. D., and Beck, H. C., *Nature*, **138**, 721 (1936).

making of today. Glass appears to have been used first as a gem, probably on a parity with natural gems, not as an imitation of them, for in these early days of glass-making the man-made product would have surpassed in rarity even the natural gems. As late as Ptolemaic times glass gems were among the most prized possessions; and even today glass is used extensively for ornamental jewelry. The glass used for the purpose by the Egyptians was usually colored. Because of its low refractive index, it lacked the brilliancy of glass now made for jewelry from the highly refractive "Strass paste."

Glass was used later for hollow vessels, especially unguent jars and small vases, which were not blown, but molded. The process was laborious and of limited scope. A core of sand was built up on a wooden or metal rod, then covered with glass by building up bit by bit with the viscous glass not much above its softening temperature. Later, probably about 1200 B.C., another technique was developed, that of pressing glass into open molds. By this means shapes such as bowls, dishes and cups, which could not be made by the sand-core process, were added to the repertory of types which were at the disposal of the glass-maker. Some of the objects made by these two processes were of surprisingly intricate design and showed excellent craftsmanship. The dress of a figured subject sometimes consisted of as many as 100 to 150 pieces of colored glass, drawn out until the threads were no more than a thousandth of an inch in thickness. In making the well-known "millefiori" glass threads of many colors were fused into a rod, so that the cross-section showed a colored pattern. This was then cut into discs, which were laid side by side and rolled into a matrix of colorless, transparent glass. The resulting mosaic was then worked up into vessels by the ordinary processes.

Transparent glass was rare, the quality of transparency not being important for the uses for which glass was intended. White opaque glass was made in the Eighteenth Dynasty by the use of tin oxide. Blue glass was used extensively; and its color usually was due to copper, which gave a turquoise blue, very different in hue from the dark cobalt blue glass common today. According to Neumann,[28] cobalt was not found in any Egyptian glass; and the only ancient glass in which it has been found is a single specimen from Nippur, dated at about 1400 B.C. Copper was also the coloring agent in red glass, but the effect obtained resembled jasper, not the copper ruby of more recent times. Green glass also was colored with copper or iron. Table I. 1 gives the compositions of a number of antique glasses, most of which represent analyses by Neumann and his co-workers.

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[28] Neumann, *B.*, *Chem. Ztg.*, **51**, 1013 (1927).

Invention of Glass Blowing

The invention of glass blowing caused an industrial revolution, which changed a luxury into a necessity. Glass had been used only for small and precious articles, but the process of blowing glass with the aid of a blowpipe made possible the production in quantity of a better and cheaper article. The time and place of the first free glass blowing is not certain. It formerly was thought to have been in the Twelfth Dynasty, because of representations at Beni Hasan, showing workmen manipulating what was thought to be a blowpipe before a fire. These so-called "blowing tubes" are now [29] known to represent blowpipes which were used for metal working; and the supposed lumps of glass, colored bright greenish-grey, were the fireclay ends of these tubes. Kisa [30] dated the invention to a little before the beginning of the Christian Era, between the end of the Ptolemaic period and 20 B.C.[31]

TABLE I. 1—Compositions of Some Antique Glasses
After Neumann

No.	SiO_2	Na_2O	K_2O	MgO	CaO	Al_2O_3	Fe_2O_3	Mn_2O_3	CuO	SO_3
1	61.70	17.63	1.58	5.14	10.05	2.45	0.72	0.47	0.32	...
2	62.71	20.26		4.52	9.16	1.47	0.96	...	...	0.92
3	63.86	22.86	0.80	4.18	7.86	0.65	0.67	trace	...	...
4	65.95	20.30	0.96	1.37	6.89	2.49	0.28	0.97	...	1.08
5	67.82	13.71	2.34	2.30	4.03	4.38	...	1.12	1.96	0.98
6	64.10	18.26	0.77	1.30	6.06	3.59	...	1.38	1.18	1.53
7	63.20	16.57	1.34	2.20	7.10	3.77	...	0.74	...	1.10
8	68.48	14.95	2.83	5.28	5.71	0.70	...	...	...	0.54
9	69.82	13.51	2.18	4.09	5.79	1.40	1.80	0.41	0.36	0.96
10	67.80	16.08	2.08	2.89	3.80	3.22	0.92	0.54	1.51	1.01
11	67.03	10.12	1.82	4.93	7.83	2.48	1.88	2.64	0.79	0.75
12	65.03	17.37	1.65	2.52	5.65	2.13	0.97	0.65	1.94	1.70
13	64.41	13.98	2.37	5.59	6.19	1.52	1.36	...	2.60	1.28
14	62.70	15.21	2.12	3.29	8.80	3.82	1.07	0.83	1.00	0.94

1. Dark blue translucent fragment, 1400 B.C., Tell-el-Amarna.
2. Light yellow translucent glass, 1400 B.C., Tell-el-Amarna.
3. Transparent red, colorless, contains bubbles, 1400 B.C., Tell-el-Amarna.
4. Colorless fragment, outside strongly decomposed, 1st to 2nd century A.D., Elephantine.
5. Dark blue translucent, 1500 B.C., Thebes.
6. Dark blue, slightly transparent Roman glass, 2nd century A.D. Also contains FeO, 1.59.
7. Dark green translucent, 1500 B.C., Thebes. Also contains FeO, 1.43; SnO_2, 1.96.
8. Window fragment, Samarra, 9th century A.D. Also contains FeO, 0.91; PbO, 0.95.
9. Rose-colored fragment, Nippur, 250 B.C.
10. Dark blue transparent, Egyptian, from Gorub Medined, 1500 B.C.
11. Deep blue transparent Egyptian, from Gorub Medined, 1500 B.C. Also contains SnO_2, 0.39.
12. Babylonian-Assyrian, Nippur, 1400 B.C. Also contains CaO, 0.93; PbO, 0.19.
13. Babylonian-Assyrian, Nippur, 1400 B.C. Also contains SnO_2, 0.32.
14. Dark blue, transparent, Egyptian, from Gorub Medined, 1500 B.C. Also contains SnO_2, 0.41.

Harden,[32] in a discussion of the glass of this period, says:

[29] Partington, J. R., "Origins and Development of Applied Chemistry"; Longmans, Green, London, 1935. Diergart, P., *Glastech. Ber.*, **14**, 422 (1936).

[30] Kisa, A., "Das Glas im Alterthum"; **1**, 206, 299, Leipzig, 1908.

[31] Neumann, B., *Z. angew. Chem.*, **41**, 203 (1928), cited evidence to show that the art of glass blowing was known in Babylon in 250 B.C.

[32] Harden, D. B., "Greece and Rome," **3**, 140 (1934).

> ". . . It was a short road thereafter that led first to blowing glass in moulds that bore elaborate patterns, and then to blowing vessels at the end of the blowpipe—in other words, free-blown glass.
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> "These developments must have occurred about the beginning of the Christian Era, and are probably due to workers on the Syrian coast. There is a group of mould-blown vases belonging to Syrian workshops of about that time, many examples of which bear signatures of artists in Greek characters as part of the moulded design. The two best names are Ennion and Artas, and their vases have been found on both eastern and western Mediterranean sites. These Syrian craftsmen were undoubtedly among the very first makers of mould-blown glasses, and it is highly probable that one of their members invented the process."

This advance in technique was accompanied by, or immediately followed by, an improvement in glass quality. While some excellent glass was made as early as the Eighteenth Dynasty, most of the antique glass was crude. The qualities of transparency and freedom from color were unimportant or undesirable for imitations of precious stones, or for inlays and plaques; but with the invention of glass blowing, and the extension in the uses for which glass was suitable, these qualities at once became desirable. The glassware of the early Roman Empire shows great improvement over that of its predecessors. Pliny[33] stated:

> "Still, however, the highest value is set on glass that is nearly colorless or transparent, as nearly as possible resembling crystal, in fact. For drinking vessels glass has quite superseded the use of silver and gold."

The rapid expansion of glass manufacture was in part the result of the invention of glass blowing, but it could not have taken place but for the commercial stability afforded by the Roman Empire. Glass manufacture spread throughout the Empire, not only to Egypt and Syria, but also to Greece, Italy and the Western provinces of Gaul and the Rhineland. There is a plentiful supply of glass of the period. The glassworkers were masters of their craft. In 220 A.D., Alexander Severus laid a tax on the glass manufacturers of Rome, who were so numerous that a section of the city was assigned to them.

Glass had become a common material of the household, used for tableware, toilet bottles, and unguent vases, for storage of wine and other liquids and for seals and signets. The first use of glass for windows was mentioned by Lactantius, at the close of the third century. The use of glass for funerary furniture reached its height in the first and second centuries A.D. The Portland vase, now in the Gold Room of the British Museum, is a splendid specimen of this period of Roman art. It was found in 1550 in a tomb of the third century A.D., but it

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[33] "The Natural History of Pliny," trans. by Bostock, J., and Riley, H. T., 6, 382, Henry G. Bohn, London, 1857.

probably was made in the first century. The scene, which is cut out of a layer of white opaque glass, stands out from a deep blue background.

There is not much information concerning glass in the period from the fall of Rome to the eleventh century. The disturbed political and social conditions consequent to the overthrow of the Roman Empire by the Germanic tribes undoubtedly caused a decadence in glass manufacture in Western Europe and the migration of the center of the industry to the Eastern Roman Empire. The comparative scarcity of glass objects in this period, as contrasted with that immediately preceding, is due also, in part, to the influence of the Christian religion in abandoning the use of funerary furniture, the source of many of the glass relics of the preceding period. No written records of Western European glass manufacture during this period are known. Heraclius, in the second half of the tenth century, gave many details concerning the manufacture of glass. It is probable that his account represents an industry which had continued from the days of the Empire. Theophilus Presbyter, in the twelfth century, gave an extended discussion of glass manufacture, a discussion which probably reflects the influence of the Venetian renaissance, superimposed on the traditions of the previous five centuries.

After the break-up of the Roman Empire, glass manufacture was carried on in the Eastern Empire. The Byzantine workers were especially adept in making colored glass and mosaics. It has been suggested that the art of making stained glass owes its origin to Greek workers of this period. If so, it soon was introduced into France, and Theophilus regarded it as a French art. Gregory von Tours (593 A.D.) and Bishop von Protus (609 A.D.) used colored glass for glazing, and a century later glass was imported to England.

Adalberon, Bishop of Rheims, used colored glass windows, designed to represent biblical scenes, when rebuilding the cathedral in 969-988 A.D. This is one of the earliest records of the use of stained-glass windows. However, it is not to be supposed that the first stained-glass windows were those at Rheims, nor that the art of making stained glass developed before the more utilitarian use of glass to keep out the weather. It is more probable that the use of glass for windows spread slowly and continuously after its introduction, and that the lack of record of such use is part of the scarcity of historical records in the period from the third to the ninth century.

These so-called Dark Ages were a period of intellectual vigor in the Islamic world, and glass manufacture benefited from the spirit of the age. It was during this period that the use of glass for weights[34] was developed to the highest accuracy by the Arabs. These apparently were not made until about 300 A.D., reached their highest accuracy about

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[34] Petrie, Sir W. M. Flinders, *Trans. Newcomen Soc.*, 5, 72 (1924-5).

780, and by 1300 had been abandoned. The manufacture of glass was mentioned by Jabir ibn Haiyan (the "Latin Geber") about 776. More research is needed on this period of the history of glass in Islam.

Probably as an indirect result of the Crusades and of the fall of the Eastern Empire, glass manufacture in Venice entered a period of development about the beginning of the eleventh century which soon made that city the center of the glass industry, which dominant position it maintained for at least four centuries. The phrase "Venetian glass" still is used to designate a type of blown ware, and the name is still sometimes associated with a tradition of quality. Glass manufacture in Venice became a large-scale industry, which was jealously protected as a monopoly. An elaborate guild system was set up in 1279, which provided for a system of apprenticeship requiring eight years for its completion. In 1291 the glass works were moved to the island of Murano, a separate borough of the city, and drastic measures were taken to prohibit the exportation of scrap glass, called cullet, and the emigration of workmen.[35] Syrian craftsmen were imported, who brought with them technical recipes and procedures from Byzantium and the Egyptian orient. The technical excellence of the Venetian glassware gives evidence of the highest degree of craftsmanship, and the beauty of its design has never been surpassed. New types of ware were developed, notably the crackled ware. The art of "silvering" mirrors with mercury was known in Venice in 1369, although not invented there, and Venetian mirrors were for many years the standard of excellence.

Although glass manufacture probably persisted in many places through the Dark Ages, it spread rapidly from Venice in the following centuries. Concerning this period we have much information. Technical details of glass manufacture and furnace construction were given by Agricola.[36] Of special importance is the book by Neri, "L'Arte Vetraria,"[37] published in Florence in 1612, later reprinted and annotated by Merrett and Kunckel, which is a treasure-house of glass history. Here are described the use of lead oxide and of borax, which did not become common glass constituents until later, and of arsenic oxide as fining agent. Several colored glasses are described, including the most splendid of all, gold ruby.*

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[35] "Three days after, I returned to Venice, and passed over to Murano, famous for the best glass in the world, where, having viewed their furnaces, and seen their work, I made a collection of divers curiosities and glasses, which I sent to England by long sea. It is the white flints from Pavia, which they pound and sift exceedingly small, and mix with ashes made of a sea-weed brought out of Syria, and a white sand, that causes this manufacture to excel." "Diary of John Evelyn" (Everyman's Library, No. 220); J. M. Dent, London; E. P. Dutton, New York. The extract deals with the year 1645.

[36] Hoover, H. C. and L. H., "Georgius Agricola, De Re Metallica"; London, 1912.

[37] Neri, A., "L'Arte Vetraria"; Florence, 1612; 2nd edition, 1661; reprinted in Venice, 1678; Latin tranlation, Amsterdam, 1668 and 1686; English translation by Merrett, 1662; German edition, 1679 and 1689; French translation, 1752.

* See footnote, Chapter XVI, p. 438.

The Modern Period in Glass Manufacture

This great work by Neri, "L'Arte Vetraria," was the beginning of the scientific approach in glass technology. While science in its modern sense was still far in the future, and while the scientific treatment of the problems of glass technology is largely the accomplishment of this generation, nevertheless the basis was laid in the assembly of facts in this monumental volume. Neri was a priest, and presumably his interests were largely academic. Merrett, an English physician and a member of the Royal Society, brought to the work not only the technique of a different nation, but also the critical viewpoint of a scientist. Kunckel, a glass-maker of no mean scientific ability, descended from a family of glass-makers, brought not only a further development in technique, but also the practical touch which made "L'Arte Vetraria" a classic of chemical technology.

From this period the development of glass was rapid. Factories multiplied in Europe, and glass became more and more a part of every man's life. In 1600 the art of cut glass was developed. In 1615 the use of coal instead of wood for fuel was discovered in England. Another English invention, flint glass, was made in 1675. "Flint glass" is a term having two different meanings. Sometimes it merely refers to any clear glass, for example clear glass bottles used for dispensing drugs. The flint glass invented in 1675 is a type containing lead oxide as its characteristic ingredient. The name "flint glass" comes from the use of a pure silica in the form of flint by the early makers. In the later development of optical glass, the term "flint" came to be applied to glasses possessing a higher refractive index and greater dispersive power than the "crown" glasses, as indicated in Fig. XVI. 10. The optical flint glasses contain lead oxide.

The awakening interest in chemistry manifested in the eighteenth century naturally included glass, but the inhibiting influence of the phlogiston theory, based on an erroneous conception of calcination and combustion, prevented any theoretical progress. Sir Isaac Newton, in 1681, replaced lead oxide by zinc oxide. A real advance in this period was made in the selection and purification of raw materials. In addition, Swab and later Scheele and Lavoisier investigated the chemical durability of glass when exposed to the corroding action of water and of weak acids.

In the progress of glass manufacture during the nineteenth century, the type known as optical glass played an important part. Glass used for optical instruments of precision is a small part of the total glass production; yet the developing of glass sufficiently perfect to meet the exacting requirements of optical instruments of precision has contributed enormously to our knowledge of glass technology, and has played an important part in the development of all types of glass. It differs from ordinary glass in two particulars.

One difference is its freedom from physical imperfections. It must be free from unmelted particles, or "stones," from bubbles, and from chemical inhomogeneity, which gives rise to regions of variable refractivity, known as "cords" or "striae"; and it must be thoroughly annealed. Chemical homogeneity is obtained by stirring the molten glass, a process discovered about 1790 by a Swiss watch-maker, Pierre-Louis Guinand. The process was long kept a profound secret. His son, Henri Guinand, became associated in Paris with Bonteps, director of the glassworks of Choisy-Le-Roi. The partnership was not successful, and in 1848 political troubles caused Bonteps to go to England, where he became associated with Chance Brothers, who still are among the best-known manufacturers of optical glass. Henri Guinand continued the manufacture of optical glass in Paris with great success. He was followed by his grandson, M. Feil, and later by Ch. Feil, who became associated with E. Mantois; and this association later developed into the famous glass house of Parra-Mantois. Thus, both the invention and the development of a homogeneous glass suitable for optical purposes were due to Guinand and his descendants. The necessity of chemical homogeneity in glass for optical purposes was manifest, but it is only recently that its desirability in ordinary glass has become evident; and improvement in this respect of all types of glass is now receiving attention from manufacturers.

The second characteristic of optical glass is the wide range of refractive index and dispersion. The designing of lenses capable of producing undistorted images requires the use of glasses differing in their optical properties; and in the search for such glasses extensive studies on the effect of the incorporation of new ingredients have been made. This systematic search, begun about the beginning of the nineteenth century, has contributed largely to our understanding of glass.

Faraday's researches[38] on the manufacture of optical glass are a classic of the early period of the nineteenth century. His characterization of glass "rather as a solution of different substances one in another than as a strong chemical compound" indicates his chemical insight. Faraday worked especially with the use of boric oxide as a constituent of glass. Harcourt, later associated with Stokes, studied the modification of glass properties by a systematic variation in composition and by the introduction of new components. None of these studies led to commercial developments.

The outstanding study of the properties of glass as affected by composition was that of O. Schott; and this study inaugurated a new period in

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[38] Faraday, M., *Trans. Roy. Soc. (London)*, part 1, 1 (1830); "Experimental Researches in Chemistry and Physics," 231-291, London, 1859.

TABLE I. 2—Properties of Some Multi-component Glasses *

Table III. 4	Type	Density g/cm^3	Young's modulus Unit = 1 kilobar; 1 bar = 14.50 lb./in.^{2} = 1.020 kg/cm^2	Poisson's ratio	Tensile strength	Compressive strength	Thermal expansion $\frac{10^6}{l}\frac{\Delta l}{\Delta t}$	Specific heat g-cal/g
	Pyrex chem. resistant	2.25	611				3.2 (19–350°)	0.20
1	496/644	2.370[1]	715[2]	0.197[4]	0.68[1]	12.4[1]		0.204[2]
56	Thermometer, 59^{III}	2.370[1]	711[2]				5.90 (0–100)[6]	
3	506/602	2.5[3]	644[2]	0.221[4]				
4	511/640	2.47[3]	731[2]	0.210[4]				
6	513/637	2.47[3]	781[2]	0.213[4]			7.97 (17.5–94.7)[5]	
7	513/573	2.572[3]	637[2]	0.226[4]	0.83[1]	9.6[1]		
9	516/536	2.6[3]		0.219[4]				
10	517/609	2.49[3]	704[2]				8.83 (18.7–90.5)[6]	
11	517/602	2.580[1]	647[2]	0.231[4]	0.66[1]	9.0[1]	9.63 (17–95.5)[5]	
25	571/430		598[2]	0.222[4]			7.93 (12.9–97.6)[5]	
27	573/576	3.21[3]	727[2]	0.252[4]			7.90 (18.9–93.1)[5]	
34	610/574	3.532[1]	783[2]	0.271[4]	0.73[1]	8.3[1]		0.140[2]
40	645/341	3.879[1]	535[2]	0.224[4]	0.53[1]	8.3[1]		
43	751/276	4.731[1]	537[2]	0.239[4]	0.52[1]	6.6[1]		
46	905/217	5.944[1]	499[2]	0.261[4]	0.35[1]	5.9[1]	9.33 (24.5–84)[5]	
55	165^{III}	2.479[1]	717[2]		0.82[1]	11.1[1]		0.196[2]
57		2.378[1]	704[2]		0.80[1]	9.7[1]		
58			621[2]	0.221[4]				
59		2.629[1]	651[2]		0.66[1]	9.7[1]		
61	Thermometer, 16^{III}	2.585[1]	732[2]	0.228[4]			8.03 (14.6–92.2)[6]	
63		2.424[1]						0.209[2]
64		2.518[1]	589[2]	0.253[4]	0.77[1]	6.7[1]		0.189[2]
65		2.480[1]						0.204[2]
66		2.668[1]	573[2]	0.261[4]	0.81[1]	7.2[1]		
67		2.848[1]	709[2]				4.57 (12.69–89.8)[6]	0.162[2]
68		3.578[1]	528[2]		0.60[1]	7.6[1]		
	Borate glasses							
48	507/614	2.243[1]	461[2]	0.274[4]	0.57[1]	8.0[1]	6.71 (14.4–94.4)[5]	0.218[2]
50	523/614	2.238[1]		0.273[4]				0.232[2]
52	653/508	3.527[1]	801[2]	0.319[4]			3.33 (10.35–92.9)[5]	0.166[2]
53	666/392	3.691[1]						0.136[2]
	Phosphate glasses							
70	516/700	2.588[1]					9.30 (17.7–92.7)[5]	0.190[2]
71	522/697	2.588[1]	664[2]	0.235[4]	0.55[1]	7.0[1]		
72	558/670	3.070[1]	620[2]	0.253[4]	0.75[1]	7.4[1]	8.70 (20.3–92.2)[5]	0.159[2]
75	567/656	3.238[1]		0.272[4]				0.146[2]

* Composition references are to Table III. 4, except Pyrex chemical resistant glass, which is Table III. 3, No. 20.

[1] Winkelmann, A., and Schott, O., *Ann. Physik Chem.*, **51**, 697 (1894).

[2] Winkelmann, A., *Ann. Physik Chem.*, **49**, 401 (1893).

[3] Zschimmer, E., in Doelter, C., "Handbuch der Mineralchemie," 1, 869; Dresden and Leipzig, 1912.

[4] Straubel, R., *Ann. Physik Chem.*, **68**, 369 (1899).

[5] Pulfrich, C., *Ann. Physik Chem.*, **45**, 609 (1892).

[6] Hovestadt, H., "Jena Glass," Macmillan, New York, 1902.

the history of glass. He was associated with E. Abbé, whose insight into the qualities necessary for the improvement of optical systems, and whose genius for making use of the new glasses developed by Schott, contributed largely to the success of the association and of the famous glass house of Schott und Genössen at Jena. Also associated with Schott was Winkelmann, whose studies on the mechanical properties of glass as affected by their composition produced a wealth of data which is still unequalled. The measurements of Table I. 2, made on glasses whose compositions are given in Table III. 4, are largely the result of the collaboration of Schott and Winkelmann.

More recent developments can be considered only briefly. The revolution in glass manufacturing methods which has taken place in the twentieth century, especially in the last two decades, has transformed the industry from one dependent on the skill of the individual workman, working under crude conditions and with a material imperfectly understood, to one dominated by continuous machine production, precisely controlled by the application of scientific methods.

The methods used in the manufacture of glass are those made necessary by the high temperatures required to melt the ingredients and by the corrosive action of the molten glass on the containers, especially during the reaction period. The best materials available for both furnaces and containers for melting glass are refractories containing as their essential constituents silica, the preponderating oxide in most glasses, and alumina, a common glass constituent. The refractory is dissolved by the glass, and the process tends to continue until the refractory is destroyed. In recent years the life of glass-makers' refractories has been greatly increased by replacing the traditional refractories, containing from 20 to 40 per cent alumina, and made of clay or similar materials, by the newer "mullite" type, containing 70 per cent or more of alumina.

In primitive times melting was done in clay pots heated by a wood fire; and the wood-burning furnaces used in Egypt during the Eighteenth Dynasty, although smaller, resembled those described by Theophilus, Agricola and Neri. With increasing technical competence the design of the furnaces for burning wood was improved; then, as the forests became depleted, coal was substituted for wood, and this was replaced in turn by natural gas and oil. Melting pots gradually increased in size from those used by the early Egyptians, which were only two or three inches in depth and diameter,[39] to modern plate-casting pots holding upwards of three tons of glass.

Today most glassware made on a large scale is manufactured by automatic machines, and fed from tank furnaces, in which the furnace itself serves as a container for the fluid glass. Such furnaces are of

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[39] Petrie, Sir W. M. Flinders, "Tell-el-Amarna," 18, Methuen, London, 1894.

either the regenerative or recuperative type, fired by gas or oil, with the fuel ports arranged along the sides or at one end so as to direct the flames out over the glass pool. The whole is covered with a low refractory roof, either domed or arched. The raw materials are fed in at one end of the tank, and the glass withdrawn at the other. A partition or "bridge wall" usually separates the tank into a "melting end" and a "working end." A "throat" through the bridge wall connects the two ends under the surface of the glass. Those parts of the tank which are in contact with the molten glass are made of refractory pieces known as flux blocks, which must be as resistant as possible to the corrosive action of the glass. This problem of corrosion resistance probably has been solved more successfully for tank blocks than for pots used in the intermittent melting process.

Pot melting of glass is used at present only in the smaller hand-production factories, or for special glasses made in small quantity or requiring an oxidizing atmosphere. In most operations the pot is used repeatedly until destroyed by solution or breakage. Almost all optical glass is made in pots, a new one being used for each melt. In the manufacture of plate glass by this method, the pot of glass is removed from the furnace, the contents either poured onto an iron casting table and rolled to uniform thickness with an iron roller, or flowed onto large power-driven rollers through which the plate flows onto a moving table beneath. The plate is then annealed, ground and polished. Most plate glass today is drawn in continuous sheets directly from a tank.

Until recently, window glass was made by hand either by the "Crown" or the cylinder process. In the Crown process, a large, somewhat spherical, globe was blown on a pipe. Opposite the pipe the globe was flattened, and a solid iron rod, called a punty, was fastened to the flat part. The neck of the globe was cracked off at the pipe, after which the glass, supported by the punty, was re-heated. By rapid rotation the globe was opened gradually and turned outward until a flat disc of glass was produced, an operation requiring great skill and manual dexterity. The disc was placed then on a bed of warm sand, the punty detached, the disc transferred to an annealing oven, and, after cooling, cut into square or rectangular panes. The thick section to which the punty was attached was the "bull's-eye," which is now sought by collectors.

In the cylinder process, the blower made a large cylinder, which was split open and flattened by re-heating. This process was superseded by one in which larger cylinders were drawn by machine, and split open as before. The cylinder process has been replaced largely by flat drawn glass, drawn directly from the tank in a continuous sheet. This is an illustration of a common trend in the mechanization of the glass industry. The hand process was replaced first by a machine which imitated, often in great detail, the methods used by the hand operative. This machine was replaced in turn by far more efficient processes which, disregarding precedent, and utilizing to the full the characteristic properties of glass, obtained the desired result by much simpler methods.

The manufacture of hollow ware, one of the large branches of the glass industry, is almost entirely mechanized. Bottles, fruit-jars, tumblers, lamp chimneys, lantern globes, electric light bulbs and radio tubes are made by machine on an enormous scale. Heavy ware, such as signal lenses, cooking ware, flat plates and electrical insulators is pressed in cast-iron or alloy-steel molds, into which the glass is fed either by hand or by automatic feeders. Standard shapes of laboratory ware often are made by machine, but special apparatus is fashioned by the glass-blower.

The period since the World War has been especially productive in advances in the glass industry, both in improvements in technical processes and methods, and in the increase in our knowledge of the fundamental scientific background of glass technology. Much of this increase in knowledge was the direct product of the enforced extension of the optical glass industry during the War. Optical glass is one of the key materials of civilization, and during the War it was recognized as one of the essential munitions. The enormously increased requirements led to the extension of the optical glass industry, and the removal from it of the veil of mystery in which it had been deliberately enveloped since its beginning. Partly as the result of war-time necessity, and partly as the result of the appreciation by the glass manufacturers that the soundest foundation for a strong industry is the understanding of its fundamental scientific principles, there have been published extensive and thorough studies of the relation between the composition and physical properties of all kinds of glass. Studies of the phase equilibrium relations in glass-forming systems have given us an understanding of why glass can be manufactured and worked, and of what the chemical relationships are that set limits to the compositions of matter obtainable as glass.

These relationships between composition and properties form the subject matter of the subsequent chapters, in each of which the information in the literature is summarized, and to some extent discussed critically. The treatment throughout is based primarily on chemical composition, and measurements on glasses of known composition are quoted whenever possible. Much of this information deals with simple glasses, prepared to ascertain the effect of change in composition on properties, for it is only by systematic experimentation, varying but one factor at a time, that unexceptionable generalizations can be developed. Measurements on multi-component commercial glasses also have been included, especially when the composition is known. Table I. 2 contains a collection of such measurements. With the exception of Pyrex chemical resistant glass, all of these glasses were made by Schott u. Gen. at Jena, and were studied by Schott, Winkelmann and their collaborators. The compositions of these glasses are in Table III. 4A, and they are mentioned frequently in the following chapters.

The Glass Industry

Statistics of glass production in the various countries, given in Table I. 3, show the magnitude of the industry and its cosmopolitan character. These statistics were compiled by the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. They are the first attempt to obtain a world-wide statistical picture of the glass industry.

THE DEFINITION OF GLASS

In the preceding historical section a general knowledge of what glass is has been assumed. Glass is so commonplace a part of every-day experience that a definition is almost unnecessary; yet the term has been applied to such a variety of substances that some preliminary indication should be given as to the type of substance whose properties are to be considered in the following chapters.

One of the early definitions of glass was given by Merrett in the commentaries[40] accompanying his translation of Neri's "L'arte Vetraria":

> "Glaſs is one of the fruits of the fire, which is moſt true, for it is a thing wholly of Art, not of Nature, and not to be produced withnout ſtrong fires. I have heard a ſingular Artiſts merrily to this purpoſe ſay, that their profeſſion would be the laſt in the world: for when God ſhould conſume with fire the Univerſe, that then all things therein would Vitrifie and turn to glaſs. Which would be true upon ſuppoſition of a proportionable mixture of fit Salts, and Sand or Stones.
>
> " 'Tis much like all ſort of mineral or middle mineral. I find Authors differ much about referring Glaſs to it's Species. Agricola, lib. 12. de Metallis, maketh it a concrete juyce, Vincent Belluasensis, lib. 11. calls it a ſtone, Fallopius reckons it amongſt the Media mineralia, and the workmen, when it is in a ſtate of fuſion call it metall. But to me it ſeems neither of theſe, which this generall Argument ſufficiently evinceth, that all the forementioned are natural concretes, but Glass is a compound made by Art, a product of the fire, and never found in the bowels of the earth, as all the others are. . . . But to ſhorten this compariſon, I ſhall here ſet down the proprieties of glaſs, whereby any one may easily difference it from all other bodies.

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[40] Merrett, C., "The Art of Glass, written in Italian by Antonio Neri, and translated into English, with some Observations on the Author"; 208, 214, Octavian Pulleyn, London, 1662.

TABLE I. 3—Estimated World Production of Glass and Glass Products *
(Values have been converted into U. S. Dollars)

Official Statistics Unless Otherwise Noted

Producing Country	Year	Production (000 omitted) Metric Tons	Production (000 omitted) Value (U.S.$)	No. of Establishments	Employment
United States	1935	2,948 [c]	283,925	213	67,100
Germany	1935	700 [d]	132,400 [b]	300 [f]	85,100 [j]
United Kingdom	1934	775 [h]	76,000	125 [f]	43,000
Rumania	1930	500 [c]	40,000 [g]	63 [c]	6,000 [c]
Czechoslovakia	1935	148 [a]	29,000 [a]	200	22,000 [i]
France	1937	476 [c]	28,000 [c]	147 [c]	38,000 [c]
Belgium	1935	235 [a]	25,000	125 [f]	28,500 [c]
Italy	1935	100 [d]	25,000	500	28,000 [c]
Japan	1935	500 [c]	20,000	696	23,866
Soviet Russia	1935	600	11,000 [k]		71,000
Canada	1935	75 [h]	10,000	68	3,100
Sweden	1935	65	7,156	58	5,000
Australia	1937	85 [g]	7,000 [c]	3	4,000 [c]
Poland	1935	97	6,000	60	10,000
Netherlands	1935	75 [c]	5,000 [c]	10 [c]	5,000 [c]
Yugoslavia	1931	45 [c]	3,500 [c]	6 [c]	1,500 [c]
Denmark	1935	25 [h]	2,000	5	1,163
Norway	1936	12	1,350	5	855
China	1933	15 [c]	1,144 [c]	40 [c]	4,000 [c]
Spain	1935	30 [e]	1,000 [e]	150 [c]	(m)
Portugal	1935	10 [c]	1,000 [c]	7 [c]	(m)
Austria	1926	10 [c]	4,000 [c]	10 [c]	2,500 [c]
Latin America	1935	100 [c]	11,000 [c]	105	17,000 [c]
Total (estimated)		8,000	800,000	3,000	500,000

Basis of Estimates:

[a] Known relationship to exports.
[b] Fuel activity in relation to previously compiled data.
[c] Trade estimates.
[d] Value per ton as indicated by exports.
[e] Known relationship to imports.
[f] Lists of manufacturers.
[g] Metric ton valued at $80.
[h] 140 per cent of sand consumption.
[i] 54 per cent of average (40,000).
[j] 85 per cent of 1928 total.
[k] Unofficial domestic rate of ruble $.03.
[m] No basis for estimate.

World Trade in Glass *
(Values converted into U. S. $1,000)

Country of Export	1929	Per cent of Total World's Exports	1936	Per cent of Total World's Exports	Approximate Per cent of Local Production
Germany	59,014	29	55,387	41	40
Czechoslovakia	40,804	20	24,138	18	80
Belgium	42,023	21	18,641	14	75
United States	10,931	5	8,264	6	3
United Kingdom	11,000	5	7,800	6	10
Japan	6,090	3	7,438	5	40
France	21,281	10	5,870	4	20
Austria	2,287	1	2,187	2	50
Netherlands	3,557	2	1,742	1	35
Italy	2,032	1	1,109	1	4
Sweden	1,221		1,062	1	14
U. S. S. R.	2,200	1	720		6
China	600		372		30
Australia	175		320		5
Others (estimated)	1,765		450		
Total (estimated)	205,000		135,500		

* From "World Production and Trade in Glass"—Bureau of Foreign and Domestic Commerce, U. S. Department of Commerce.

"1 'Tis a concrete of ſalt and ſand or ſtones.

2 'Tis Artificial.

3 It melts in a ſtrong fire.

3 When melted 'tis tenacious and ſticks together.

4 It wasts not no conſumes in the fire.

5 'Tis the laſt effect of the fire.

6 When melted it cleaves to Iron, &c.

7 'Tis ductile whilſt red hot, and faſhionable into any form, but not malleable, and may be blown into a hollowneſs.

8 Breaks being thin without annealing.

9 'Tis friable when cold, which made our proverb, As brittle as glaſs.

10 'Tis diaphanous either hot or cold.

11 'Tis flexible and hath in threeds motum rectitutionis.

12 Cold and wet diſunites and breaks it, eſpecially if the liquors be ſaltiſh, and the glaſs suddainly heated.

13 It onely receives ſculpture, and cutting, from a Diamond or Emery ſtone.

14 'Tis both coloured and made Diaphanous as pretious ſtones.

15 Aqua fortis, Aqua Regis, and Mercury, diſſolve it not as they do Metalls.

15 Acid juyces nor any other thing extract either colour, taſt, or any other quality from it.

16 It receives poliſhing.

17 It loſeth nor weight, nor ſubſtance, with the longeſt and moſt frequent uſe.

18 Gives fuſion to other Metalls and ſoftens them.

19 Receives all variety of colours made of Metalls both externally and internally, and therefore more fit for Painting than any other thing.

20 'Tis the most plyable and faſhionable thing in the world, and beſt retains the form given.

21 It may be melted but 'twill never be calcined.

22 An open glaſs fill'd with water in the Summer will gather drops of water on the outſide, ſo far as the water reacheth, and a mans breath blown upon will manifeſtly moiſten it.

23 Little balls as big as a Nut fill'd with Mercury, or water, or any liquor, and thrown into the fire, as alſo drops of green glaſs broken fly aſſunder with a very loud & moſt ſharp noiſe.

24 Wine Beer nor other liquors will make them muſty, nor change their colour nor ruſt them.

25 It may be cemented as Stones and Metals.

26 A drinking Glaſs fill'd, in part with water (Being rub'd on the brim with the finger witted.) yields Muſical notes, higher or

> lower, according as 'tis more or leſs full, and makes the liquour frisk and leap."

"The Century Dictionary"[41] gives: "A substance resulting from the fusion of or combination of silica (rarely boracic acid) with various bases. It is usually hard, brittle, has a conchoidal fracture, and is more or less transparent, some kinds being entirely so."

The "New Standard Dictionary"[42] gives: "A fused mixture of silica, usually in the form of natural sand, and two or more alkaline bases such as soda, lime, or potash. It is generally transparent or translucent, is brittle and sonorous at ordinary temperatures, and when heated becomes soft and ductile, finally melting. The point of fusion varies with its composition. It breaks with a conchoidal (commonly called vitreous) fracture, and is acted on by hydrofluoric acid, but not by ordinary solvents."

"Webster's Dictionary"[43] gives: "An amorphous substance, usually transparent or translucent, consisting ordinarily of a mixture of silicates, but in some cases of borates, phosphates, etc." Since one of the meanings of "amorphous" is given as "uncrystallized," the similarity in structure between ordinary liquids and glass might be inferred.

The statements included in the above definitions are correct, except that which implies that glass has a "point" of fusion. The statements concerning composition are empirical and too restrictive, and in the second definition exclude one-component glasses such as silica glass, and even two-component glasses, such as the sodium silicates. None of them brings out the essential continuity of condition from the fluid melt at high temperatures to the rigid glass at ordinary temperatures.

Transparency is frequently considered a characteristic of glass, yet much commercial glassware is either translucent or opaque. It is always true, however, that the lack of transparency is caused by the fact that some material, usually crystalline, is dispersed or suspended in a glassy matrix, itself transparent. The material may be a colloidal dispersion, as in a gold or copper ruby glass; or a suspension of submicroscopic to microscopic particles, as in some opaque glasses; or microscopic crystals ranging in size from the lower limits of resolving power to fairly coarse crystals, as in some opals and white glasses. In all these cases, however, the material is essentially glassy, and to exclude such commercial products from the category of glasses would be futile.

Other products contain much glassy material, but are not considered as glasses. Any hard-fired brick contains some glass, and a glassy bond[44] is almost universal in ceramic materials. The finest porcelains

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[41] "The Century Dictionary"; The Century Co., New York, 1914.

[42] "Funk and Wagnalls New Standard Dictionary"; Funk and Wagnalls Co., New York, 1932.

[43] "Webster's New International Dictionary"; G. and C. Merriam, 2nd. ed., Springfield, Mass., 1935.

[44] Morey, G. W., *J. Am. Ceram. Soc.*, 17, 145 (1934).

contain a large percentage of glass, and glazes and enamels are essentially glassy, yet there is no suggestion that such products should be considered as glassware.

The organic glass substitutes are excluded from consideration because they differ so greatly in composition, methods of manufacture, and properties from those substances that have always been known as glass, that they constitute a separate division of chemical technology.

Discussion of the definition of glass usually centers around whether at ordinary temperatures glass is an undercooled liquid or an amorphous solid, which places the emphasis on the definition of liquid and solid, rather than on the properties of the substance to be defined. The chief difficulty in connection with the definition not only of glass, but also of liquid and of solid is that the terms used either are themselves not well defined, or are commonly used with a much looser meaning than is allowable for the purpose of a definition. The necessity for precision of meaning in scientific discussion results in one of two evils: either a word commonly used in every-day speech is assigned a strange and rigid meaning, or even worse, a new word is coined.

Glass is manifestly solid, in the usual sense of the term. The definition of solid, however, is not easy. The fact that a substance is solid to the touch is not a sufficient criterion; and the more closely one inquires into the properties characteristic of a solid, the more one is forced to depart from the popular conception and resort to greater and greater abstraction. In scientific discussion, moreover, solid has two different and unrelated meanings.

In the first of these meanings, solid is spoken of as one of the three contrasting states of matter, solid, liquid and gaseous. Each of these states usually is capable of precise delimitation in respect to the others; and the relation between these states, in both simple and complex systems, is the subject-matter included under the study of phase equilibrium. In the development of that subject, it may have been unfortunate that new terms, which were not commonplaces of every-day speech, were not adopted in place of "solid" and "liquid," with their many irrelevant connotations. To attempt to change the vocabulary of the subject now would be Quixotic. The mere substitution of the term "crystalline" for solid would not help the non-specialist, for to him "crystalline" may mean only clear and limpid, *e. g.*, the crystalline sky! To be sure, most people rarely come into contact with any solid-liquid transition except ice-water, and here there is no confusion between the two completely unrelated concepts. But considered as a state of matter, "solid" means "crystalline," a phase characterized by the atoms being in a fixed, regularly repeated, geometrical pattern, as contrasted with the haphazard arrangement of the liquid phase.

When a crystalline solid is heated to its melting point,* it changes to a liquid, or to a mixture of liquid and a different crystalline solid; and on cooling the reverse phase changes take place. The materials which always have been called glasses are characterized by the property that when melted at high temperatures and cooled, they do not devitrify, that is, they do not undergo the discontinuous change into the stable aggregate of crystalline phases ** which equilibrium would require. At high temperatures during melting they are ordinary liquids, and like other liquids, will flow under the influence of gravity or other small force. At the temperatures at which they should freeze or begin to crystallize, the glasses are viscous liquids, and it is largely because of their great viscosity that glasses can be cooled through their freezing points without devitrification. They then become "undercooled liquids." As undercooling is continued to ordinary temperature, the glasses become increasingly viscous. The increase in viscosity with decreasing temperature is a continuous process† from the liquid above the melting or freezing point to the rigid glass at ordinary temperatures; and from the freezing point to ordinary temperatures, the material remains an undercooled liquid with respect to the process of crystallization. Glass is in a condition which is analogous to, and continuous with, the liquid state, but which, as the result of having been cooled from a fused condition, is characterized by so high a degree of viscosity as to be for all practical purposes rigid. It is solid, but not in the sense of being in the "solid" or "crystalline" state.

In its other meaning, solid is defined in terms of certain physical properties; and here again is met the difficulty that the popular and the precise meanings of most of the words used differ greatly. A solid is rigid; but rigidity is measured in terms of a modulus, a relation between stress and strain, which may range within wide limits. A solid is hard; but hardness is a concept that never has been defined in such terms that it can be measured. A definition of "solid" in terms of physical properties requires the choice of properties which can be measured and the setting of limits to those properties. It is not sufficient to say that a solid is hard and rigid; limiting values must be set to the properties included in the definition or the term is not defined.

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* The complications introduced by a vapor phase and by variations in pressure are omitted as not pertinent to the discussion.

** See the discussion in Chapter II on *The Devitrification of Glass*. The "melting temperature" is the temperature to which the ingredients are heated during manufacture, which is determined primarily by the necessity of getting the melt fluid enough to free itself from bubbles in a short time. At the melting temperature the glass is usually too fluid for the subsequent shaping operations, and must be cooled until the requisite viscosity has been reached at the "working temperature." The "melting point," "freezing point," or "liquidus temperature" is the temperature at which crystals can exist in equilibrium with the melt, and ordinarily is many degrees below both the melting and the working temperatures.

† See the discussion of the "stabilization" of glasses, p. 268.

In applying such a definition of solid to a material such as glass, the additional difficulty is encountered that the physical properties change with temperature and composition, and arbitrary values set for the dividing line between liquid and solid can be reached by change in temperature or composition, or both. But the several physical properties do not change in the same degree with change in composition or temperature; and if a set of simultaneous values of physical properties reached by heating a given composition is chosen as the dividing line between liquid and solid, that same set of values may not be simultaneous for another composition. Thus it becomes necessary either to impose an arbitrary set of limiting values for hardness, strength, rigidity, viscosity and electrical and thermal conductivity for every composition, or to take one property, such as viscosity, and to call a liquid everything having a viscosity less than, a solid everything having a viscosity greater than, that limit.

If one insists on that definition of solid which ignores crystallinity and lays stress on physical properties such as rigidity, the definition of glass as an amorphous solid would become logical and consistent, provided the definition were restricted to ordinary temperatures. The difficulty comes when it is attempted to tell when the glass ceases to be a solid and becomes a liquid. It must be admitted that to call window-glass liquid, rather than solid, conflicts with one's natural regard for the fitness of things. But this reaction is the expression of instinctive opposition to the use of terms in a sense different from that ordinarily used in speech and literature. Opposition will be aroused even more by the following quotation: "Glass and pitch are familiar examples of very viscous liquids. Paint, clay slip, and thin mud in a similar manner must be classified as soft solids."[45] The dilemmas are caused, not by calling glass a liquid or a solid, but by the impossibility of logically and completely defining and delimiting "solid" in terms of physical properties. Without doubt, the conception of glass as an undercooled liquid is more in accord with experiment, and leads to fewer dilemmas when the concept is followed to its logical conclusion.

An ordinary glass is considered best as an undercooled liquid, or as second choice, as an amorphous solid, using the two terms as possessing almost equivalent connotation. There appears to be no justification for considering the "glassy state" as a "fourth state of matter." Such a concept in no way clarifies the contradictions which have been considered, and introduces new problems of definition difficult to solve. Moreover, all attempts at precise definition of glass are confused by the custom, not to be condemned, of referring to the material as glass, not only at ordinary temperatures, or at intermediate temperatures, as when one speaks of the annealing temperature, or of the softening tem-

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[45] Bingham, E. C., "Fluidity and Plasticity," 214, McGraw-Hill, New York, 1922.

perature of glass, but also at high temperatures when the material is in an undoubtedly liquid condition to which the preceding discussion does not apply. Thus experimental work discussed in the chapters on viscosity and surface tension was done mostly with glasses which satisfied the ordinary concept of a liquid which flows immediately under the action of a small force.

One circumstance has been omitted in the above discussion which is of importance in defining glass in the broadest sense, but which is not of importance in respect to any known glass. Most substances are so fluid at their freezing points that crystallization cannot be prevented; they cannot be obtained as glass. A few substances have sufficient viscosity at their freezing points to make it possible to cool them as glasses. The essential thing is not that the liquid can be cooled below its freezing point without a discontinuous change taking place, but that it can be cooled until its viscosity has increased to such an extent that it forms a serviceable glass. With silicate glasses this happens to be far below their freezing points, but there is no necessary or known relation between freezing point and viscosity, and there is no *a priori* reason why some substance should not acquire the necessary viscosity above its freezing point. The above considerations are, however, hypothetical, as there is no glass known which is above its freezing point at ordinary temperature.

A definition which makes use only of those characteristics which are essential to glass is the following: A glass is an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of that substance, but which, as the result of having been cooled from a fused condition, has attained so high a degree of viscosity as to be for all practical purposes rigid.

Chapter II

The Devitrification of Glass

All glasses on cooling from the melting temperature pass through a temperature or temperature range in which the liquid becomes unstable with respect to one or more crystalline compounds, and at and below this temperature the glass can be devitrified, that is, crystallized, by appropriate heat treatment. If during the working or annealing processes the glass is held too long in the temperature region in which crystallization takes place most readily, it will devitrify and be ruined. Devitrification is the chief factor which limits the composition range of practical glasses, and it is an ever-present danger in all glass manufacture and working, and takes place promptly with any error in composition or technique.

In discussing the devitrification of glass it is important not to confuse the equilibrium phase-relationships with the tendency of the glass to crystallize, and the speed with which crystallization takes place once the process is started. These kinetic factors will be considered in detail subsequently; but the phase equilibrium relationships are the only factors which admit of exact definition and precise determination.

When a complex glass is cooled, at some temperature the melt becomes saturated with a crystalline phase, just as a salt solution on cooling becomes saturated with salt; and if undercooling does not take place, crystals will separate. The temperature at which this process begins is known as the liquidus temperature. When a devitrified glass is heated, and at each temperature sufficient time is given for enough crystals to dissolve to saturate the liquid, the crystals will gradually and continuously decrease in amount, and finally disappear. The temperature at which the last trace of crystals disappears also is the liquidus temperature; and experiments in which the liquid is cooled give the same temperature for the liquidus as experiments in which the devitrified glass is heated.

Phase equilibrium diagrams represent the relation between composition and temperature with reference to the melting and crystallizing process in mixtures containing several components. They offer a means of expressing in compact and graphic form a large amount of information of a type which is fundamental to the comprehension of many factors vital to ceramic engineering and glass technology. The information thus available is apparent at a glance to those familiar with such diagrams, but a considerable amount of thought and study and actual use is necessary to attain such a degree of competence. In the following discussion two phase-equilibrium diagrams will be considered in detail, and several others of interest in connection with the devitrification of glass will be reproduced with little discussion. The diagrams chosen for detailed discussion are of soda-silica and of soda-lime-silica, fundamental to the common soda-lime-silica glasses.

Much of the subsequent discussion is based on purely geometrical relationships, and it is pertinent to inquire into the reason for this intimate connection between geometry and chemistry. It arises in part in the methods used in expressing composition by means of geometrical figures; but in larger part in the thermodynamic relationships underlying the study of heterogeneous equilibrium. The entire structure on which is based the study of heterogeneous equilibrium is due to the genius of J. Willard Gibbs, and is developed in detail in his "Equilibrium of Heterogeneous Substances."[1] In that paper the application of the first and second laws of thermodynamics was extended to substances containing independently variable components, in contrast to the previous restriction to substances of invariable composition. One consequence of that treatment is the Phase Rule. In its usual form this rule is but an incidental qualitative consequence of equations which express relationship between those quantities which connect the thermodynamic stability of the different phases with their composition. These equations may be applied either analytically, or, as is commonly done, graphically.[2] Gibbs himself showed how to make a graphic representation of the stability relationships of phases of both fixed and variable composition, by means of curves and surfaces; and, indeed, the use of the equilateral triangle for representing composition in three-component systems is due to Gibbs. As will be seen later, a triangular phase equilibrium diagram representing a three-component system is divided into various fields or regions by boundary curves, and these boundary curves represent the projection on the basal plane of curves obtained by the intersection of surfaces representing the limits of thermodynamic stability, as expressed by the fundamental equations of the various phases. It is from a consideration of the fundamental equations, or of the surfaces of thermodynamic stability derived from them, that the various theorems are derived which govern our application of geometric laws to the chemical relationships expressed in phase equilibrium diagrams.

Gibbs' derivation of the Phase Rule may be summarized as follows:

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[1] "The Scientific Papers of J. Willard Gibbs," 1, 55, Longmans, Green, 1906. See also section G, "The Phase Rule and Heterogeneous Equilibrium" by Morey, G. W., in "Commentary on the Scientific Writings of J. Willard Gibbs," 1, Yale University Press, 1936.

[2] Morey, G. W., *J. Phys. Chem.*, 34, 1745 (1930).

Application of the first and second laws of thermodynamics to a phase consisting of n components leads to the equation

$$vdp = sdt + m_1\, d\mu_1 + \ . \ . \ . + m_n\, d\mu_n$$

for the relation between the variables for changes taking place in an isolated system. In this equation v is the volume and s the entropy of the $m_1 + \ . \ . \ . \ m_n$ units of the components making up the phase; p and t are the pressure and the temperature of the phase; and $\mu_1 \ . \ . \ . \ \mu_m$ are values for each component of an intensity factor called the chemical potential. The components are those chemical substances which may be regarded as the simplest or the most convenient set from which all the phases can be derived. For example, a mixture having the molecular composition $Na_2O + 3\ CaO + 6SiO_2$ can be regarded as made up from the components $Na_2O \cdot 2\ SiO_2$, $CaO \cdot SiO_2$, and SiO_2, or from $Na_2O \cdot SiO_2$, $CaO \cdot SiO_2$, and SiO_2, or from Na_2O, CaO, and SiO_2, and the choice is one of convenience.

The concept of phase and the derivation of the Phase Rule result from the application of the above equation to the consideration of "the different homogeneous bodies which can be formed out of any set of component substances." "It will be convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its quantity or form. We may call such bodies as differ in composition and state different phases of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase. Phases which can exist together, the dividing surfaces being plane, in an equilibrium which does not depend on passive resistances to change, we shall call coexistent."

Each one of a set of coexistent phases will be characterized by an equation of the form given above, containing $(n + 2)$ variables, namely, the n chemical potentials, pressure and temperature. When there are $(n + 2)$ coexisting phases, evidently the condition of the system will be determined completely. An example is the coexistence of three phases, ice, liquid and vapor, at the triple point of water. When there are $(n + 1)$ phases, there can be a single variation or "degree of freedom," producing a monovariant system; when there are n phases, there are two degrees of freedom, producing a divariant system. In general, if F represents the number of degrees of freedom, C, the number of components, and P, the number of phases,

$$F = C + 2 - P.$$

For example, in the binary system H_2O–KNO_3, coexistence of two phases, liquid and vapor, can take place over a range of composition, temperature and pressure; fixing the composition alone does not fix the temperature or the pressure, nor does fixing either pressure or temperature fix the composition. The system is divariant. If the composition of the solution becomes such that crystalline KNO_3 separates, coexistence of three phases, solid, liquid and vapor, still can take place over a range of composition, pressure and temperature; but fixing any one of these fixes the other two. The system is monovariant. If the solution be cooled until ice separates, four phases coexist, and the pressure, temperature, and composition of the liquid are fixed. The system is invariant.

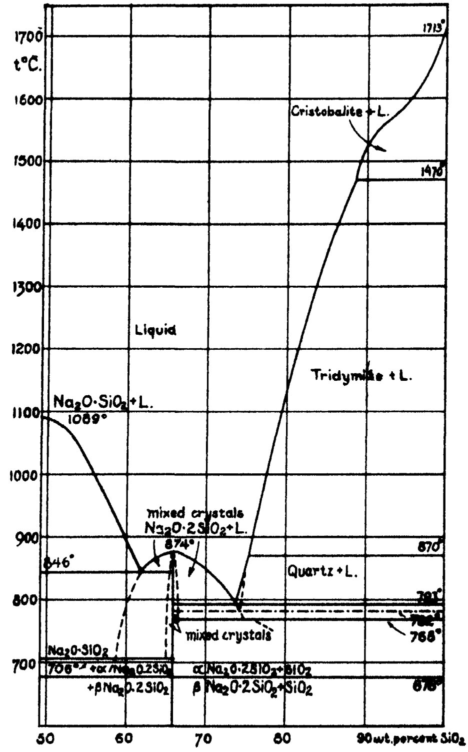

FIGURE II. 1.—Phase Equilibrium Diagram of the Binary System Na_2O-SiO_2. Composition Is Expressed as Percentage by Weight of SiO_2. After Morey, Bowen and Kracek.

Two-component Systems

The first system to be discussed is that formed by sodium metasilicate and silica,[3] shown in Fig. II. 1; the properties of the compounds are given in Table II. 1; and the temperature and composition of the invariant points are in Table II. 2. The vertical scale in Fig. II. 1

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[3] Morey, G. W., and Bowen, N. L., *J. Phys. Chem.*, **28**, 1167 (1924). Kracek, F. C., *J. Phys. Chem.*, **34**, 1583 (1930).

represents temperature; the horizontal scale represents composition. This is part of the larger system Na_2O–SiO_2, and the composition is given in percentage of SiO_2 by weight, considering Na_2O as the other component. The designation of the components in such a case is largely a matter of convenience. $Na_2O \cdot SiO_2$ and SiO_2 could as well have been chosen as components, as was done by Morey and Bowen in their original paper, and the phase relationships are equally well shown by such a choice. Also, the composition could have been expressed in molecular percentage, using either Na_2O or $Na_2O \cdot SiO_2$ as components, and that again is a matter of convenience. Since Na_2O and SiO_2 have molecular weights so nearly equal, their relation as components would give a diagram almost identical with that obtained by the form of representation used in Fig.

Table II. 1—Properties of Crystalline Compounds

Compound	Melting reaction (r) or inversion (i) temp., (°C.)	Crystal habit	Crystal system	2V	Optical character	Refractive Indices α ω	β	γ ε
SiO_2, low quartz	573 *i*	bipyramids	hexagonal		uniax. pos.	1.544		1.553
SiO_2, high quartz	870 *i*							
SiO_2, low tridymite	1470 *i*	plates	pseudo-hexagonal	35°	biax. pos.	1.473	1.47	1.469
SiO_2, low cristobalite	1713	plates	pseudo-cubic		uniax. neg.	1.487		1.484
$Na_2O \cdot SiO_2$	1089	needles	ortho-rhombic	large	biax. neg.	1.513	1.520	1.528
$Na_2O \cdot 2SiO_2$	874	plates, needles	ortho-rhombic	50–55°	biax. neg.	1.497		1.508
$K_2O \cdot SiO_2$	976	granular	ortho-rhombic	35°	biax. pos.	1.520		1.528
$K_2O \cdot 2SiO_2$	1045	plates	ortho-rhombic	large	biax. neg.	1.503		1.513
$K_2O \cdot 4SiO_2$	770	plates	mono- or triclinic	large	biax. pos.	1.477		1.482
β-$CaO \cdot SiO_2$ (wollastonite)	1150 *i*	needles	monoclinic	39°	biax. neg.	1.616	1.629	1.631
α-$CaO \cdot SiO_2$ (pseudo-wollastonite)	1540	hexagonal plates	hexagonal		uniax. pos.	1.610		1.654
$PbO \cdot SiO_2$ (alamosite)	764	prisms	monoclinic	65°	biax. neg.	1.947	1.961	1.968
$2PbO \cdot SiO_2$	743		?	80°	biax. neg.	2.13	2.15	2.18
α-$4PbO$-SiO_2	725 *r*	irregular plates	?	40°	biax. pos.	2.31	2.34	2.38
$2Na_2O \cdot CaO \cdot 3SiO_2$	1141 *r*	octahedra	isometric			$n = 1.571$		
$Na_2O \cdot 2CaO \cdot 3SiO_2$	1284	equant	?			1.595		1.598
$Na_2O \cdot 3CaO \cdot 6SiO_2$ (devitrite)	1060 *r*	prisms	ortho-rhombic	75°	biax. pos.	1.564	1.570	1.579
$K_2O \cdot CaO \cdot SiO_2$	1630		hexagonal		uniax. pos.	1.600		1.605
$2K_2O \cdot CaO \cdot 3SiO_2$	1005 *r*	octahedra	pseudo-cubic			$n = 1.572$		
β-$K_2O \cdot 3CaO \cdot 6SiO_2$	1020 *i*	needles, plates	ortho-rhombic		biax. neg.	1.56		1.57
α-$K_2O \cdot 3CaO \cdot 6SiO_2$	1115 *r*	prisms	ortho-rhombic	large	biax. pos.	1.575		1.59
$2K_2O \cdot CaO \cdot 6SiO_2$	959	plates	mono- or triclinic		biax. neg.	1.540		1.544
$4K_2O \cdot CaO \cdot 10SiO_2$	946	plates	hexagonal		uniax. neg.	1.548		1.537
$K_2O \cdot 2CaO \cdot 9SiO_2$	1050 *r*	prisms, plates	mono- or triclinic	large	biax. neg.	1.515		1.535
$K_2O \cdot 2PbO \cdot 2SiO_2$	918				uniax. neg.	1.93		1.72
$K_2O \cdot 4PbO \cdot 8SiO_2$	779					1.69		1.79
$K_2O \cdot PbO \cdot 4SiO_2$	757			75°	biax. pos.	1.590	1.612	1.650
$2K_2O \cdot PbO \cdot 3SiO_2$	735 *r*				biax. pos.	1.685		1.665

II. 1; but if mole percentage were used with $Na_2O \cdot SiO_2$ and SiO_2 as components, the resulting diagram would have appeared distorted, because of the high molecular weight of $Na_2O \cdot SiO_2$. Whatever the choice of components, however, the point representing a given composition is the center of gravity when the quantities of the two components corresponding to that composition are placed at the ends of the axis of abscissa. This question of representation by mole per cent and weight per cent will be reverted to subsequently.

Application of the Phase Rule to this system of two components at constant pressure shows that coexistence of three phases gives an invariant system; two phases, a monovariant system; and one phase, a divariant system. The region inscribed "liquid" above the various freezing point curves, in Fig. II. 1, represents a divariant system, in which neither composition nor temperature is fixed by any of the properties under consideration. At a temperature above the liquid and solid surface a whole series of unsaturated liquids may exist, and a given composition may be liquid over a wide range of temperatures. But when such a liquid cools to the temperature represented by a freezing point curve, another phase makes its appearance, and the system loses one degree of freedom. If a liquid containing 80 per cent SiO_2 is cooled, at about 1135° crystals of tridymite (the form of crystalline SiO_2 stable from 870° to 1470°) separate, and this temperature is uniquely determined by fixing the composition. Only one liquid can coexist with tridymite at 1135°. If a mixture of tridymite and glass, of a gross composition richer in Na_2O than 20 per cent, is held at 1135°, the crystals will all dissolve, and the point in the diagram representing that composition at that temperature will be in the divariant field of liquid alone. If the mixture has a gross composition richer in SiO_2 than 80 per cent, but contains a larger proportion of crystals than corresponds to equilibrium, tridymite will dissolve until the liquid has exactly the composition 20 per cent Na_2O, 80 per cent SiO_2. The point representing this composition lies within the field "Tridymite-liquid," every point of which represents a mixture of these two phases. The composition of the solid phase is constant; the change in composition of the liquid is shown by the freezing point curve; and the relative proportions of the two phases in any mixture represented by a point in this field are given by the inverse ratio of the length of the portions into which this point divides the horizontal distance from the liquidus to the SiO_2 side of the figure. For example, if the temperature is such that the liquid contains 78 per cent SiO_2, and the gross composition of the mixture is 80 per cent SiO_2, it will consist of 20 parts of liquid and 2 parts of tridymite; but if the gross composition is 98 per cent SiO_2 the proportions will be 2 parts of liquid, of the same composition as before, and 20 parts of tridymite.

Corresponding to every liquid composition there is one temperature at which it can coexist in equilibrium with crystals, and that temperature is called the liquidus temperature. The liquidus curve of a given compound is an example of a monovariant system, because fixing either one of the variables, temperature or composition, fixes the other. The intersection of two such monovariant curves results in the coexistence of three phases, two solid and one liquid. Such a system is invariant; hence both temperature and liquid compositions are fixed. Three types of invariant points found in this system will be considered in detail. One of these is illustrated by the intersection of the quartz liquidus and the tridymite liquidus at 870°. Here the invariant point is a maximum temperature for one of the crystalline phases, quartz; a minimum temperature for the other phase, tridymite; and liquid is stable both above and below the invariant point. The chemical composition of the two solid phases is the same, and this type of invariant point is called an inversion point; if there is no solid solution, as is true in this case, the temperature is independent of the presence of the liquid phase, or of the complexity of that liquid. Of similar type are the tridymite-cristobalite inversion at 1470° and the α-β inversion of $Na_2O \cdot 2SiO_2$ at 678°, shown in Fig. II. 1.

Another type of invariant point is illustrated by the intersection of the quartz and the sodium disilicate melting-point curves. This intersection takes place at 793° and a liquid composition of 73.9 per cent SiO_2. Here the liquid is intermediate in composition between the two solid phases, and whenever the liquid phase can be made up by mixing the two coexisting solid phases the invariant point is a point of minimum temperature for liquid, and is called a eutectic. The metastable $Na_2O \cdot 2SiO_2$-tridymite eutectic shown at 782°, 74.6 per cent SiO_2, affords an example of phases persisting under conditions in which they are unstable, a phenomenon frequently met with in silicate systems, and not uncommonly occurring with more reactive substances. Another eutectic is that between $Na_2O \cdot SiO_2$ at 846° and 62.1 per cent SiO_2.

A liquid containing 50 per cent SiO_2 will begin to freeze at 1088°, and as cooling continues, and as $Na_2O \cdot SiO_2$ continues to separate, the composition of the liquid will follow the freezing point curve of sodium metasilicate until the eutectic is reached. At an intermediate temperature any mixture in the field "$Na_2O \cdot SiO_2 + L$" will be either all liquid, if the temperature is above the liquidus for the composition in question, or a mixture of liquid and $Na_2O \cdot SiO_2$ crystals, if below the liquidus. For example, a mixture containing 58 per cent SiO_2 will be all liquid above 955°; at 955° it will begin to crystallize; at 900° it will be a mixture of (60–58) parts $Na_2O \cdot SiO_2$ crystals, (58–49.21)[4] parts liquid. When the eutectic is reached the mixture will consist of (62.1–58) parts

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[4] The liquid phase at 900° contains 60 per cent SiO_2, and the compound $Na_2O . SiO_2$ contains 49.21 per cent SiO_2.

$Na_2O \cdot SiO_2$ and (58–49.21) parts eutectic liquid. Then $Na_2O \cdot 2SiO_2$ crystallizes out at constant temperature, and the mixture solidifies completely to a mixture of (65.96–58) parts $Na_2O \cdot SiO_2$ and (58–49.21) parts $Na_2O \cdot 2SiO_2$.

There are two congruent* melting points, that of the compounds $Na_2O \cdot SiO_2$ at 1089°, and that of $Na_2O \cdot 2SiO_2$ at 874°. These may be considered as two-component invariant points, in which the necessary number of equations to completely determine all the variables is given by the fundamental equations of the two coexisting phases, liquid and crystalline, and by the additional equation expressing the equivalence of composition of these two phases.

The preceding discussion has assumed that equilibrium is reached in all the phase reactions; and in the study which established the diagrams every precaution was taken to insure that equilibrium was reached. The methods which were used in studying the phase equilibrium relationships in the sodium silicate system are characteristic of those used in all such studies and are different from those commonly used. With salts and metals, the phase transformations may be followed by means of heating or cooling curves. When such materials are heated at a uniform rate, an absorption of heat takes place when melting begins, which is indicated by the temperature of the charge falling behind that of the furnace, or even remaining constant. Because of the slowness of the melting process in devitrified glasses, as well as in many other complex silicate melts, no indication of the beginning of melting can be found on the heating curve; and, indeed, some substances may even be superheated for a short time many degrees above the temperature of melting without much formation of liquid. This condition is, of course, unstable and, if held for a long time above the requisite temperature, the crystals will dissolve; but overheating is a common occurrence. Similarly, on cooling the glass does not crystallize (that is why it remains a glass) and hence the type of discontinuity which gives so marked an effect in the freezing of metal cannot be observed. If held long enough, however, and at an appropriate temperature, crystals will separate. Accordingly the "quenching" method is used in studying such mixtures. A few milligrams of the material, wrapped in thin platinum or gold foil, are held at a known constant temperature long enough for equilibrium to be reached, which may be a matter of hours, days, or even weeks. Then the charge is cooled in such a manner as to freeze the equilibrium, and is examined with the petrographic microscope; if all glass, the temperature of heat treatment was above the liquidus; if a mixture of glass and crystals, it was below the liquidus; and by successive heat treatments the liquidus temperature may be located as closely as desired. By measuring the properties of the crystals they

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* Cf. p. 54.

can be positively identified. With difficult mixtures it is customary to have two charges side by side, one initially glass, the other previously crystallized. The heating must be continued long enough for both charges to attain the same condition.

With the exception of compositions near the disilicate-quartz eutectic there is little difficulty in reaching equilibrium in the system $Na_2O \cdot SiO_2$, and over most of the composition range maintaining the charge at constant temperature for an excessive time is not required. The crystallization process, even though well under way, is quickly checked by slow cooling, and it is easy to obtain any desired intermediate stage. Sodium metasilicate can be studied either by the quenching method or by the heating curve method. It crystallizes so readily that large melts cannot be cooled as glass, but always crystallize. On the other hand, it undercools to such as extent that the cooling curve method is not

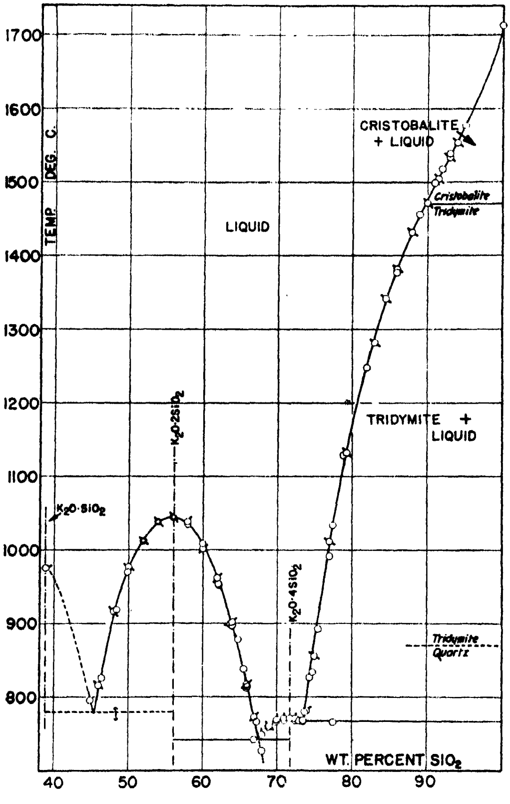

FIGURE II. 2.—Phase Equilibrium Diagram of the Binary System K_2O-SiO_2. After Kracek, Bowen and Morey.

reliable. Sodium disilicate is not difficult to crystallize, at least not in comparison with many commercial glasses; yet thousands of tons of glass of that composition had been made without obtaining the compound, and it was unknown before the work of Morey and Bowen. Special attention should be called to the $Na_2O \cdot 2SiO_2$-quartz eutectic. There is here a remarkable melting point lowering; addition of 25 per cent of Na_2O lowers the melting point from 1710° to 793°, almost 1000°. The low temperature of this eutectic is of the first importance to glass technology. Glass of this composition would be excellent were it not easily attacked by water, and hence not stable in moist air. It is, of course, essential that glass be stable not only on exposure to the air but also under far more drastic treatment; and for this reason other oxides must be added to improve the chemical durability of this eutectic, if a stable glass is to be obtained. Nevertheless, about a half million tons of sodium silicate glass of essentially this composition are manufactured annually for use in the soluble silicate industry, and devitrification troubles are unknown. To crystallize mixtures near this eutectic it is necessary to hold the charge just below the eutectic temperature for a long time, and the last stages of the devitrification take place even more slowly than the initial formation of crystals.

The Binary System K_2O-SiO_2

The phase equilibrium relations in the binary system K_2O-SiO_2[5] are summarized in Fig. II. 2 and Tables II. 1 and 2. The region near the composition $K_2O \cdot 4SiO_2$ is of special importance in glass technology. Over a range of composition the liquidus temperature is low, the viscosity at the liquidus is high, and the glasses are very difficult to crystallize. Potassium silicate has a limited industrial application as potash water glass, and the system is of fundamental importance to some branches of ceramic manufacture, notably of those glasses and enamels containing lead oxide.

The Binary System CaO-SiO_2

The part of the phase equilibrium diagram[6] from the composition $CaO \cdot SiO_2$ to SiO_2 is shown in Fig. II. 3. $CaO \cdot SiO_2$ is found in nature as the mineral wollastonite; the form stable at temperatures above 1150°,[7] called pseudo-wollastonite, is more commonly met with as a devitrification product of glass, and often separates in the upper part of the stability range of the low-temperature form.

On addition of SiO_2 to the eutectic between $CaO \cdot SiO_2$ and SiO_2,

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[5] Morey, G. W., and Fenner, C. N.,, *J. Am. Chem. Soc.*, **36**, 215 (1914); *Z. anorg. allgem. Chem.*, **86**, 305 (1914); Morey, G. W., and Fenner, C. N., *J. Am. Chem. Soc.*, **39**, 1178 (1917); Kracek, F. C., Bowen, N. L., and Morey, G. W., *J. Phys. Chem.*, **33**, 1857 (1929), **41**, 1183 (1937).

[6] Rankin, G. A., and Wright, F. E., *Am. J. Sci.*, **39**, 1, p. 5 (1915); Greig, J. W., *Am. J. Sci.*, **13**, 1, p. 18 (1927).

[7] Bowen, N. L., Schairer, J. F., and Posnjak, E., *Am. J. Sci.*, **26**, 193 (1933).

the melting temperature rises rapidly, until at 1698° a second liquid layer of almost pure silica is formed. This unmixing is not pertinent to glass technology, because addition of small amounts of Na_2O, K_2O, or Al_2O_3 causes the disappearance of the region of immiscibility. Liquid immiscibility is met with in other systems containing regions of possible or commercial glass compositions, but in no case are the two composition regions near each other; and every case of supposed separation of a commercial glass into two immiscible layers which has been brought to my attention has been one of inadequate mixing.

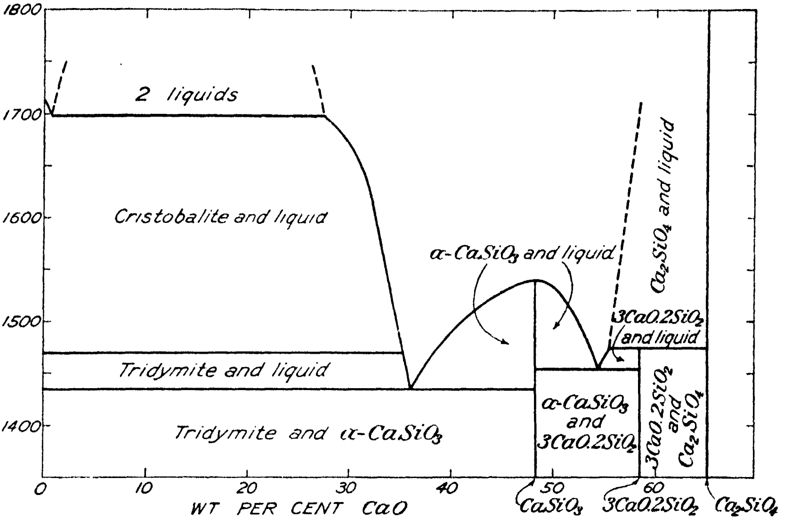

FIGURE II. 3.—Phase Equilibrium Diagram of the Binary System CaO-SiO_2. After Rankin and Wright, revised by Greig, and by Bowen, Schairer and Posnjak.

The Binary System PbO-SiO_2

The binary system PbO-SiO_2, important as an end-member of the lead glasses and as a constituent of glazes and enamels, has been studied by several investigators.[8] The most recent study is by Geller, Creamer, and Bunting,[9] and their results are reproduced in Fig. II. 4, and Tables II. 1 and II. 2. The compound $PbO \cdot SiO_2$ is found as the mineral alamosite. The compound $4PbO \cdot SiO_2$, which melts incongruently at 725° C., apparently occurs in three forms: the α-form, stable above 720° C.; the β-form, stable from 720° to about 155° C.; and the γ-form,

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[8] Cooper, H. C., Shaw, L. I., and Loomis, H. E., *Am. Chem. J.*, **42**, 461 (1909); Hilpert, S., and Weiller, P., *Ber.*, **42**, 2969 (1909); Hilpert, S., and Nacken, R., *Ber.*, **43**, 2565 (1910); Cooper, H. C. Kraus, E. H., and Klein, A. A., *Am. Chem. J.*, **47**, 273 (1912); Krakau, K. A., and Vakhrameev, N. A., *Keram. i. Steklo*, **8**, (1), 24 (1932).

[9] Geller, R. F., Creamer, A. S., and Bunting, E. N., *J. Research Natl. Bur. Standards*, **13**, 237 (1934).

TABLE II. 2—Invariant Points in Binary and Ternary Systems

	Reaction	Temp. (°C.)	Composition of liquid (Percentage by weight)		
	1. *System Na_2O-SiO_2*		Na_2O		SiO_2
1.	$Na_2O \cdot SiO_2 + Na_2O \cdot 2SiO_2 = L$	846	37.9		62.1
2.	$Na_2O \cdot 2SiO_2 + SiO_2$ (quartz) $= L$	793	26.1		73.9
3.	SiO_2 (quartz) $= SiO_2$ (tridymite)	870	24.5		75.5
4.	SiO_2 (tridymite) $= SiO_2$ (cristobalite)	1470	11.3		88.7
	2. *System K_2O-SiO_2*		K_2O		SiO_2
1.	$K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 = L$	780	54.5		45.5
2.	$K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 = L$	742	32.4		67.6
3.	$K_2O \cdot 4SiO_2 + SiO_2$ (quartz) $= L$	769	27.5		72.5
4.	SiO_2 (quartz) $= SiO_2$ (tridymite)	870	25.1		74.9
5.	SiO_2 (tridymite) $= SiO_2$ (cristobalite)	1470	10.3		89.7
	3. *System CaO-SiO_2*		CaO		SiO_2
1.	$CaO \cdot SiO_2 + SiO_2$ (tridymite) $= L$	1436	36.1		63.9
2.	Liquid $L_1 + SiO_2$ (cristobalite) $=$ liquid L_2	1698	27.5(L_1) 0.6(L_2)		72.5 99.4
	4. *System $PbO \cdot SiO_2$*		PbO		SiO_2
1.	$PbO = L$	886	100		0
2.	α-$4PbO \cdot SiO_2 = PbO + L$	725	93.3		6.7
3.	β-$4PbO \cdot SiO_2 = \alpha$-$4PbO \cdot SiO_2$	720			
4.	β-$4PbO \cdot SiO_2 + 2PbO \cdot SiO_2 = L$	714	91.78		8.22
5.	$2PbO \cdot SiO_2 + PbO \cdot SiO_2 = L$	716	84.6		15.4
6.	$PbO \cdot SiO_2 + SiO_2$ (quartz) $= L$	722	70.4		29.6
	5. *System Na_2O-CaO-SiO_2*				
	(*a*) Binary join $Na_2O \cdot SiO_2$-$CaO \cdot SiO_2$		Na_2O	CaO	SiO_2
1.	$Na_2O \cdot SiO_2 + 2Na_2O \cdot CaO \cdot 3SiO_2 = L$	1060	46.0	4.5	49.5
2.	$2Na_2O \cdot CaO \cdot 3SiO_2 = Na_2O \cdot 2CaO \cdot 3SiO_2 + L$	1151	38.2	12.0	49.8
3.	$Na_2O \cdot 2CaO \cdot 3SiO_2 + CaO \cdot SiO_2 = L$	1280	12.4	36.5	50.1
	(*b*) Binary join $Na_2O \cdot 2SiO_2$-$Na_2O \cdot 2CaO \cdot 3SiO_2$				
1.	$Na_2O \cdot 2SiO_2 + Na_2O \cdot 2CaO \cdot 3SiO_2 = L$	862	32.5	3.0	64.5
	(*c*) Ternary invariant points				
1.	$Na_2O \cdot SiO_2 + Na_2O \cdot 2SiO_2 + 2Na_2O \cdot CaO \cdot 3SiO_2 = L$	821	37.5	1.8	60.7
2.	$Na_2O \cdot 2SiO_2 + 2Na_2O \cdot CaO \cdot 3SiO_2 = Na_2O \cdot 2CaO \cdot 3SiO_2 + L$	827	36.6	2.0	61.4
3.	$Na_2O \cdot 2SiO_2 + Na_2O \cdot 3CaO \cdot 6SiO_2 = Na_2O \cdot 2CaO \cdot 3SiO_2 + L$	760	24.3	5.2	70.7
4.	$Na_2O \cdot 2SiO_2 + Na_2O \cdot 3CaO \cdot 6SiO_2 + SiO_2$ (quartz) $= L$	725	25.0	5.0	70.0
5.	SiO_2 (quartz) $+ Na_2O \cdot 3CaO \cdot 6SiO_2 + L = SiO_2$	870	18.6	7.1	74.3
6.	$Na_2O \cdot 3CaO \cdot 6SiO_2 + Na_2O \cdot 2CaO \cdot 3SiO_2 = NaO \cdot SiO_2 + L$	1059	18.8	15.1	66.1
7.	$Na_2O \cdot 3CaO \cdot 6SiO_2 + SiO_2$ (tridymite) $= CaO \cdot SiO_2 + L$	1030	13.8	12.6	73.6
	6. *System K_2O-CaO-SiO_2*		K_2O	CaO	SiO_2
1.	$K_2O \cdot 2CaO \cdot 6SiO_2 + SiO_2 = \beta$-$CaO \cdot SiO_2 + L$	1080	13.3	10.8	75.9
2.	$K_2O \cdot 2CaO \cdot 9SiO_2 + K_2O \cdot 3CaO \cdot 6SiO_2 + SiO_2 + L$	1050	13.8	10.5	75.7
3.	$K_2O \cdot 2CaO \cdot 9SiO_2 + K_2O \cdot 4SiO_2 + SiO_2$ (quartz) $= L$	720	25.1	1.9	73.0
4.	$K_2O \cdot 2SiO_2 + K_2O \cdot 2CaO \cdot 9SiO_2 + K_2O \cdot 4SiO_2 = L$	720	30.8	0.9	68.3
5.	$K_2O \cdot 2SiO_2 + K_2O \cdot 2CaO \cdot 9SiO_2 + K_2O \cdot 4SiO_2 = L$	740	31.6	2.3	66.1
6.	$4K_2O \cdot CaO \cdot 10SiO_2 + K_2O \cdot 2CaO \cdot 9SiO_2 = 2K_2O \cdot CaO \cdot 6SiO_2 + L$	825	28.8	5.3	65.9
7.	$2K_2O \cdot CaO \cdot 6SiO_2 + K_2O \cdot 2CaO \cdot 9SiO_2 = K_2O \cdot 3CaO \cdot 6SiO_2 + L$	910	26.6	7.8	65.6
8.	$2K_2O \cdot CaO \cdot 6SiO_2 + \beta$-$CaO \cdot SiO_2 = K_2O \cdot 3CaO \cdot 6SiO_2 + L$	930	32.0	11.3	56.7
9.	$2K_2O \cdot CaO \cdot 3SiO_2 + 4K_2O \cdot CaO \cdot 10SiO_2 + 2K_2O \cdot CaO \cdot 6SiO_2 = L$	890	37.2	10.2	52.6
10.	$2K_2O \cdot CaO \cdot 3SiO_2 + 2K_2O \cdot CaO \cdot 6SiO_2 + \beta$-$CaO \cdot SiO_2 = L$	800	34.2	13.0	52.8
11.	$2K_2O \cdot CaO \cdot 3SiO_2 + \beta$-$CaO \cdot SiO_2 = K_2O \cdot CaO \cdot SiO_2 + L$	830	34.1	13.7	52.2
12.	$K_2O \cdot CaO \cdot SiO_2 + \alpha$-$CaO \cdot SiO_2 = 2CaO \cdot SiO_2 + L$	1180	22.5	31.0	46.5
13.	$2K_2O \cdot CaO \cdot 3SiO_2 + K_2O \cdot 2SiO_2 + 4K_2O \cdot CaO \cdot 10SiO_2 = L$	895	40.5	7.7	51.8
14.	$K_2O . SiO_2 + 2K_2O . CaO . 3SiO_2 + K_2O \cdot 2SiO_2 = L$	770	54.7	0.2	45.1
	7. *System K_2O-PbO-SiO_2*		K_2O	PbO	SiO_2
1.	$K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 + 2K_2O \cdot PbO \cdot 3SiO_2 = L$	700	46	15	39
2.	$K_2O \cdot SiO_2 + 2K_2O \cdot PbO \cdot 3SiO_2 = K_2O \cdot 2PbO \cdot 2SiO_2 + L$	?	40	26	34
3.	$K_2O \cdot 2SiO_2 + 2K_2O \cdot PbO \cdot 3SiO_2 = K_2O \cdot 2PbO \cdot 2SiO_2 + L$	725 ?	37	27	36
4.	$K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 + K_2O \cdot PbO \cdot 4SiO_2 = L$	705	26	16	58
5.	$K_2O \cdot 4SiO_2 + SiO_2$ (quartz) $+ K_2O \cdot PbO \cdot 4SiO_2 = L$	?	18	19	63
6.	$K_2O \cdot PbO \cdot 4SiO_2 + ? + SiO_2$ (quartz) $= L$	690	10	39	51
7.	$K_2O \cdot PbO \cdot 4SiO_2 + K_2O \cdot 4PbO \cdot 8SiO_2 + ? + L$	700	10	43	47
8.	$K_2O \cdot 4PbO \cdot 8SiO_2 + SiO_2$ (quartz) $+ ? + L$	742	3.2	60	36.8
9.	$K_2O \cdot 4PbO \cdot 8SiO_2 + PbO \cdot SiO_2 + SiO_2$ (quartz) $= L$	730	0.5	71	28.5
10.	$K_2O \cdot 4PbO \cdot 8SiO_2 + 2PbO \cdot SiO_2 = PbO \cdot SiO_2 + L$	676	3.0	78	19
11.	$PbO + K_2O \cdot 2PbO \cdot 2SiO_2 + 4PbO \cdot SiO_2 = L$	705	1.5	91.7	6.8
12.	$K_2O \cdot 2PbO \cdot 2SiO_2 + 4PbO \cdot SiO_2 + 2PbO \cdot SiO_2 = L$	693	1.8	88	10.2
13.	$K_2O \cdot 2PbO \cdot 2SiO_2 + 2PbO \cdot SiO_2 + K_2O \cdot 4PbO \cdot 8SiO_2 = L.$	637	5.0	74.5	20.5
14.	$K_2O \cdot 2PbO \cdot 2SiO_2 + K_2O \cdot 4PbO \cdot 8SiO_2 + K_2O \cdot PbO \cdot 4SiO_2 = L$	682	11.0	59.5	29.5
15.	$K_2O \cdot 2SiO_2 + K_2O \cdot 4PbO \cdot 8SiO_2 + K_2O \cdot 2PbO \cdot 2SiO_2 = L.$	708	20.0	41.7	38.3

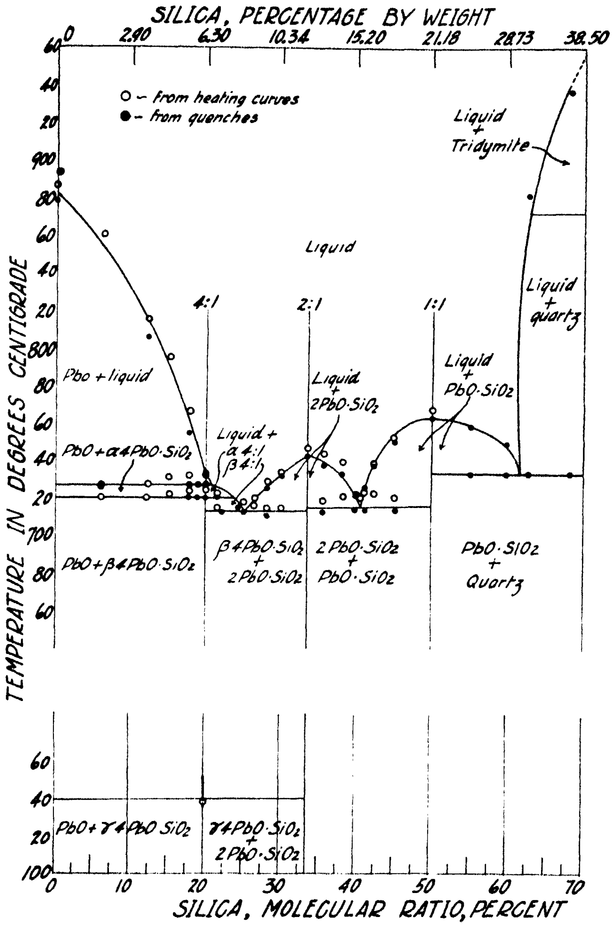

FIGURE II. 4.—Phase Equilibrium Diagram of the Binary System PbO-SiO_2. After Geller, Creamer and Bunting.

stable below about 120° C. Specimens crystallized at or below 720° C. appear as minute, probably prismatic, grains of medium birefringence and average index about 2.34. The transition between the β- and γ-forms was not located exactly, and the two forms were distinguished only by relative birefringence.

Some other binary systems of interest in glass technology are: Li_2O-SiO_2, studied by Kracek;[10] Na_2O-B_2O_3, studied by Morey and Merwin;[11] and PbO-B_2O_3, studied by Geller and Bunting.[12]

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[10] Kracek, F. C., *J. Phys. Chem.*, **34**, 2641 (1930).

[11] Morey, G. W., and Merwin, H. E., *J. Am. Chem. Soc.*, **58**, 2248 (1936).

[12] Geller, R. F., and Bunting, E. N., *J. Research Natl. Bur. Standards*, **18**, 585 (1937).

The Ternary System $Na_2O \cdot SiO_2$-$CaO \cdot SiO_2$-SiO_2

The ternary system $Na_2O \cdot SiO_2$-$CaO \cdot SiO_2$-SiO_2[12a] will be considered next. Details of this system are given in Figs. II. 5 to 9 and summarized in Tables II. 1 and 2. Figs. II. 5 and II. 6 are part of the larger equilateral triangle whose vertices represent pure Na_2O, CaO, and SiO_2. In such an equilateral triangle, the point representing a desired composition is the center of gravity of the triangle when loaded at each corner with the proportional quantities of that component. A point on a side represents a mixture containing only two components, the one represented by the opposite apex being absent; the points on a line parallel to a side represent mixtures in which the percentage of the component represented by the apex opposite that side is constant. For example, points on the side Na_2O-SiO_2 represent the binary system shown in Fig. II. 1; points on a line through SiO_2 and the compound $Na_2O \cdot 2CaO \cdot 3SiO_2$ represent mixtures in which the Na_2O:CaO ratio is 1:2; and all mixtures lying on a line parallel to the Na_2O-SiO_2 side have the same CaO content. In the figure the scale is indicated on the sides and may

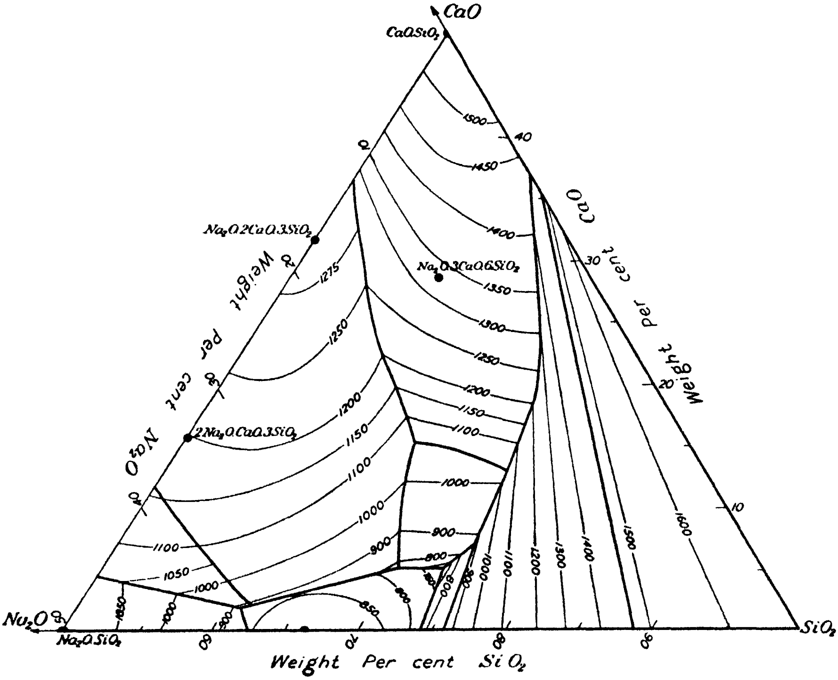

FIGURE II. 5.—Phase Equilibrium Diagram of the Ternary System Na_2O-CaO-SiO_2, showing Isotherms. After Morey and Bowen.

[12a] Morey, G. W., and Bowen, N. L., *J. Soc. Glass Tech.*, **9**, 226 (1925).

be transferred into the interior of the diagram by coördinate lines parallel to the sides. This method of representing composition in a system of three components has the advantage of symmetry and is more convenient, except when one component is present in preponderant amount, as is frequently the case with water and salt systems Other methods which can be used are discussed in detail by Roozeboom.[13]

In Fig. II. 7, right-angled coördinates are used, and this figure may be regarded as drived from Fig. II. 6 by a shear which opened out

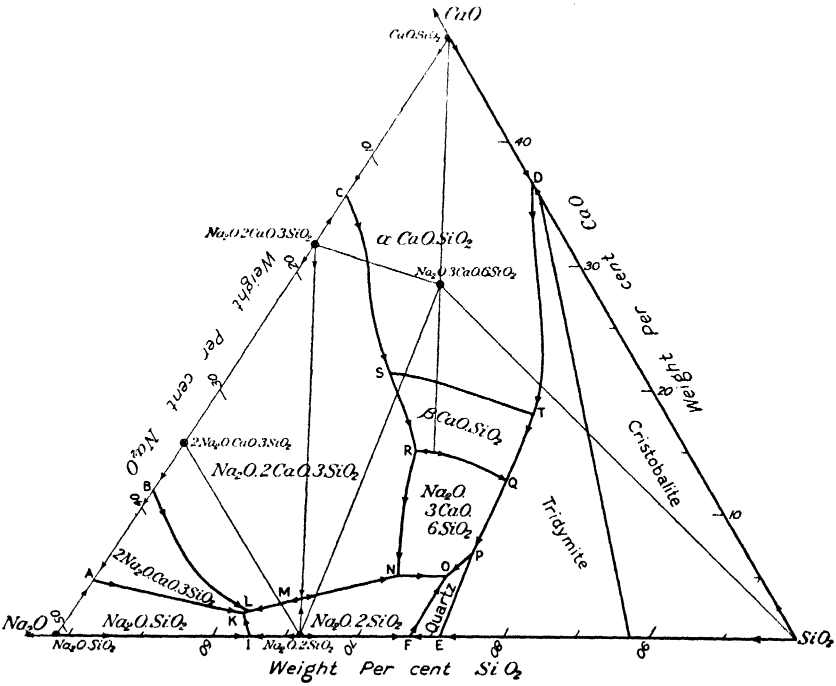

FIGURE II. 6.—Phase Equilibrium Diagram of the Ternary System Na_2O-CaO-SiO_2, showing Boundary Curves and Tie-Lines. After Morey and Bowen.

the angle opposite the side CaO-SiO_2 from 60° to 90°. In Fig. II. 8 the area included within the dashed lines of Fig. II. 7 is shown on an enlarged scale. By representing the system $Na_2O \cdot SiO_2$-$CaO \cdot SiO_2$-SiO_2 as a part of the larger system Na_2O-Ca-SiO_2, the argument along each of the sides becomes the percentage of the component oxides, the quantities determined by analysis, and directly comparable with glass compositions. Changing the method of representation by making use

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[13] Roozeboom, H. W. B., "Die heterogenen Gleichgewichte," Heft 3, Teil 1, Braunschweig, Friedr. Vieweg & Sohn, 1911.

of the two metasilicates themselves would require recalculation of every composition to the basis of the new components, and also would produce a distortion of the diagram.

Changing the method of representation from weight percentage to mole percentage also produces a distortion, in amount depending on the differences in the molecular weights of the various components. Either type of diagram can be obtained from the other by the appropriate extension or compression of the different axes, and it is important to remember that in any such distortion straight lines remain straight lines.

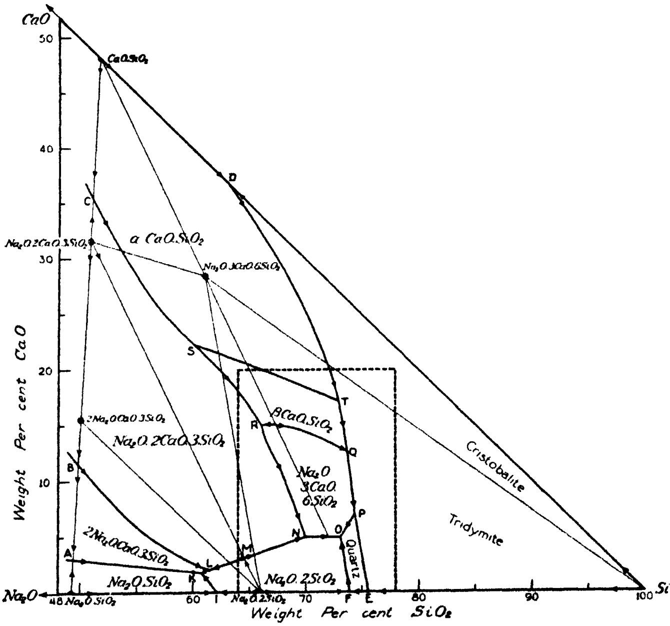

FIGURE II. 7.—Phase Equilibrium Diagram of the Ternary System Na_2O-CaO-SiO_2, represented by a Right-angled Triangle. After Morey.

A mixture of $CaO \cdot SiO_2$ and $Na_2O \cdot 2SiO_2$ remains on the straight line joining these two compounds no matter whether an equilateral or a right-angled triangle is used, or whether the oxides or any desired binary or ternary compounds are chosen as components, or whether composition is expressed in weight or mole percentage of those oxides or components. That being so, it is evident that much of the discussion in regard to the advisability of planning experiments on the variation of properties with composition by replacing a given oxide by another (for example, Na_2O by CaO) in molecular equivalent amounts, or percentage for percentage, (which amounts to keeping the ratio of the other two oxides

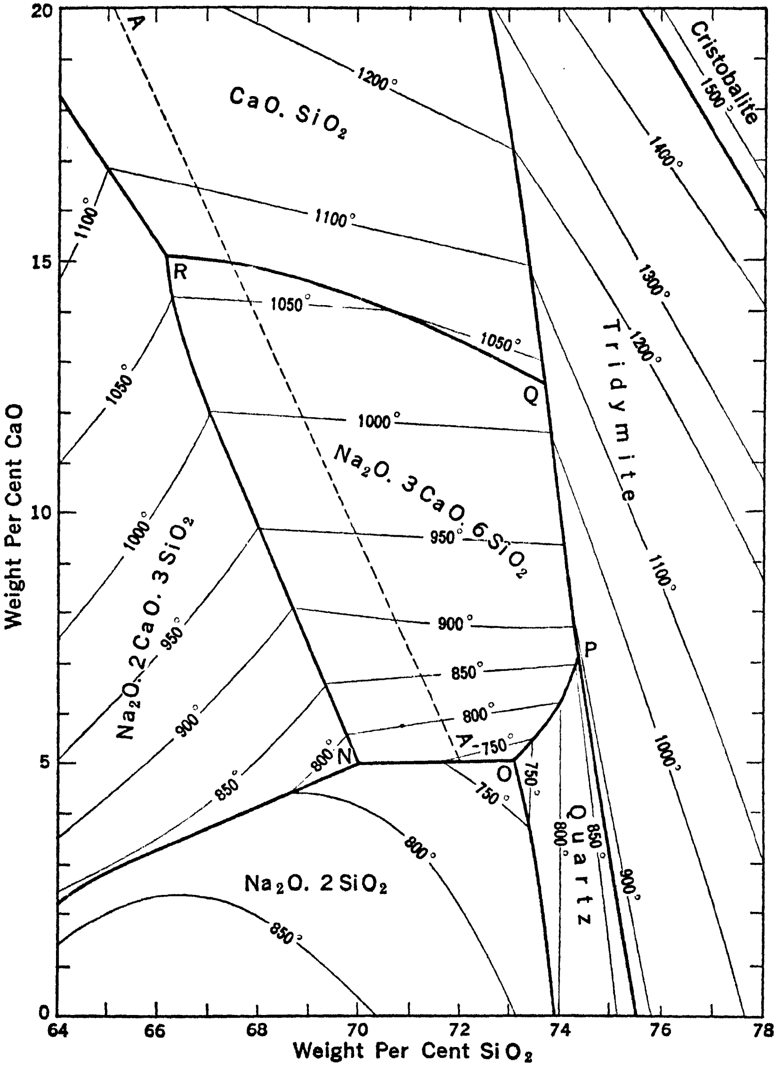

Figure II. 8.—The Isotherms and Boundary Curves in the Portion of the System Na_2O-CaO-SiO_2. Directly Applicable to Glass Technology. The weight per cent SiO_2 is indicated along the horizontal axis; weight per cent CaO along the vertical axis; weight per cent Na_2O is obtained by subtracting the sum of CaO and SiO_2 from 100. After Morey.

constant in a three-component system) or by simply adding the oxide in question to the parent glass, is pointless. In any case the variation in composition is on a straight line in the composition diagram. If the original glass, for example, is a sodium silicate glass, with the $Na_2O:SiO_2$ ratio equal to 1:3, hence containing 74.4 per cent SiO_2, on replacing Na_2O by CaO in molecular equivalent amounts, the mixtures will lie on the straight line along which the ratio $(Na_2O + CaO):SiO_2$ is 1:3, which extends from 74.4 per cent SiO_2 on the Na_2O-SiO_2 side to 76.3 per cent SiO_2 on the CaO-SiO_2 side. If the replacement is by weight percentage, the straight line is that of constant SiO_2. If CaO is added to the original glass, the composition will change along a straight line from the original sodium silicate glass to the CaO apex of the component triangle. All these types of variations, and any similar ones that may be devised, will be represented by straight lines by all such methods of representation if they are straight in one of them. It may be well to remark, in connection with such linear excursions into ternary or more complicated systems as have been discussed above, that any deductions concerning the variation of properties with composition made on the basis of such excursions must be accepted with caution. It is not possible to make sweeping generalizations as to the effect of the replacing of Na_2O by CaO on the basis of such a linear excursion into the ternary diagram. Replacing Na_2O by CaO in a trisilicate glass raises the melting point, but from that it does not follow that some other variation will not lower the melting point, and we can see from Fig. II. 5 that there is a large composition area in which the melting point is lower than that of a $Na_2O \cdot 3SiO_2$ glass.

The complete representation of the three composition variables in a plane is made possible by the additional restriction that their sum be 100 per cent, thus reducing the independent variables to two. Temperature must be expressed in a third dimension, and it is represented by the vertical distance from the base. The equilateral prism thus obtained is terminated by a complex upper surface, representing the liquidus temperatures in the various fields. A photograph of such a model is shown in Fig. II. 9. If planes parallel to the base be passed through this model at appropriate heights they will intersect the surfaces in curved lines, giving the composition of the liquidus which can coexist with the solid at that temperature, and the isotherms shown in Fig. II. 5 may be regarded as the projection of such intersections onto the basal plane.

Consider now the ternary diagrams, preferably Fig. II. 6. This diagram is divided by heavy curved lines (the projections of the valleys between the various mountain slopes of Fig. II. 9) into several fields, and the direction of falling temperature along these boundaries is indicated by arrows. Within each of the fields a different substance is the first to crystallize on cooling, or the last to dissolve on heating. For example, from all mixtures whose compositions lie within the area *BCSRNML*, the compound $Na_2O \cdot 2CaO \cdot 3SiO_2$ is the primary phase, and this area is called the field of $Na_2O \cdot 2CaO \cdot 3SiO_2$. As the liquid is cooled, and more and more of this compound separates, the composition of the residual liquid changes; and, since the crystals and the residual liquid are being formed out of the original liquid, all three compositions must lie on a straight line, with the composition of the original liquid between the other two, and dividing the line into segments inversely proportional to the relative amounts of the two phases. This is, of course, the same type of relationship that has already been discussed, with the aid of numerical examples, in the binary system.

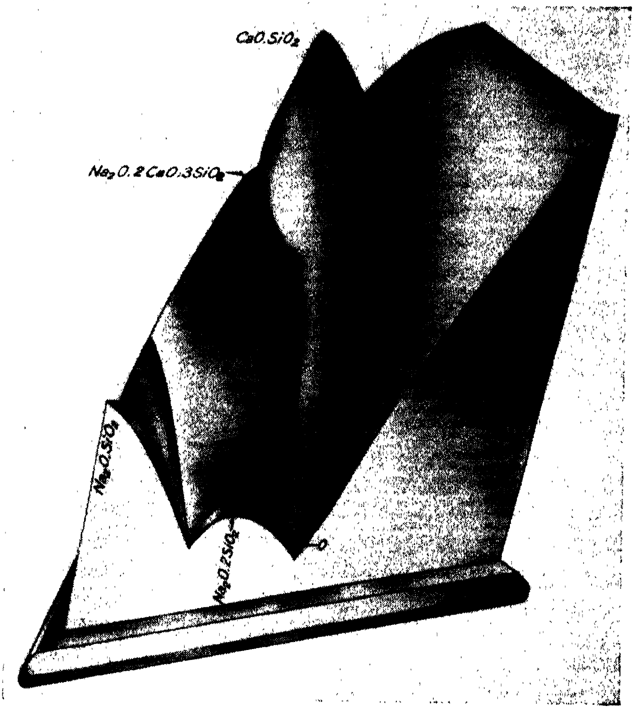

FIGURE II. 9.—Sketch of Solid Model of the Ternary System Na_2SiO_3-$CaO \cdot SiO_2$-SiO_2. After Morey.

As crystallization continues, the composition of the liquid will be continuously displaced on a straight line radiating from the composition of $Na_2O \cdot 2CaO \cdot 3SiO_2$, until that line intersects one of the boundary curves, and the system becomes monovariant. With three components at constant pressure, coexistence of two phases produces a divariant system, illustrated by the field of any compound. Divariance in this case means that at any temperature a large number of different liquids may coexist with the solid phase, and that fixing the temperature does not automatically fix the composition of the liquid. When the system becomes monovariant by the appearance of a second crystalline phase, the composition of the liquid becomes fixed when the temperature is fixed, and at any given temperature only one liquid composition can coexist with the two crystalline phases.

If the original liquid can be made up of the two crystalline phases that separate at the boundary curve, for example, if it lies on the line joining $Na_2O \cdot 2SiO_2$ with $Na_2O \cdot 2CaO \cdot 3SiO_2$ at point *M*, then it will freeze entirely at this point, and the mixture may be regarded as a binary system within the ternary system because every reaction that takes place can be expressed in terms of the two end members alone. It is important to see this distinction between those pairs of compounds which form truly binary systems, and those which do not. $Na_2O \cdot 2SiO_2$ and $CaO \cdot SiO_2$ do not form a binary system. When $CaO \cdot SiO_2$ is added to $Na_2O \cdot 2SiO_2$, the resulting compositions will follow the straight line joining these two compounds, and the phase changes which will take place can be foretold from the fields which this tie-line crosses. The liquidus temperature will first fall, while the point remains within the field of $Na_2O \cdot 2SiO_2$, but it will be seen that when a boundary is reached it is that of $Na_2O \cdot 2CaO \cdot 3SiO_2$. This compound does not lie on the tie-line in question; separation of a compound less silicic than corresponds to the tie-line must of necessity leave a liquid more silicic, and it is evident that the behavior of mixtures of these two compounds, $Na_2O \cdot 2SiO_2$ and $CaO \cdot SiO_2$, cannot be expressed without reference to the ternary system.

The composition of the compound $Na_2O \cdot 2CaO \cdot 3SiO_2$ lies within the field of this compound; a liquid of this composition will freeze completely to this compound when cooled, and when the compound is heated it shows a sharp melting point. Such a melting is called congruent. Within the same field is shown the composition of another compound, $2Na_2O \cdot CaO \cdot 3SiO_2$, but the field of this compound is represented by the area *ABLK*. Only from mixtures within this field does $2Na_2O \cdot CaO \cdot 3SiO_2$ crystallize as primary phase. When the pure crystalline compound is heated it remains unchanged until the temperature of the point *B* is reached. Then it decomposes into a liquid of the composition *B* and crystals of $Na_2O \cdot 2CaO \cdot 3SiO$; and above this temperature, and at the liquidus, this compound is the crystalline phase coexisting with liquid. Such a melting is called incongruent, and the phenomena taking place at this point are entirely analogous to those which take place at the transition point of a salt hydrate. When $Na_2SO_4 \cdot 10\,H_2O$ is heated, at its transition point it decomposes into anhydrous Na_2SO_4 and saturated solution. In the binary system, H_2O-Na_2SO_4, this is an invariant point, and indeed it is a fixed point whose equilibrium temperature is known to a high degree of accuracy. But if excess of either H_2SO_4

or NaOH be present, the temperature is no longer fixed, but is monovariant; the transition temperature of the hydrate will be lowered in either acid or alkaline solutions. The case is analogous in the silicate system. Point *B* is an invariant point in the binary system, $Na_2O \cdot SiO_2 \cdot CaO \cdot SiO_2$, but is only one point on the curve *BL*, the monovariant equilibrium $2Na_2O \cdot CaO \cdot 3SiO_2 + Na_2O \cdot 2CaO \cdot 3SiO_2 +$ liquid. It is, however, a point of maximum temperature along this curve.

Mixtures of the two compounds, $Na_2O \cdot SiO_2$ and $CaO \cdot SiO_2$, form a binary system, because the two fields crossed, those of $2Na_2O \cdot CaO \cdot 3SiO_2$ and $Na_2O \cdot 2CaO \cdot 3SiO_2$, may be regarded as fields of compounds between the two end members. Addition of $CaO \cdot SiO_2$ to $Na_2O \cdot SiO_2$ lowers the melting point of the latter, until the binary eutectic is reached at *A*. On further addition of $CaO \cdot SiO_2$, the melting point curve rises, with $2Na_2O \cdot CaO \cdot 3SiO_2$ as solid phase, until the incongruent melting point of this compound is reached, at *B*. This is an invariant point in the binary system, and the temperature remains constant until all $2Na_2O \cdot CaO \cdot 3SiO_2$ is decomposed, and the only crystals left are those of $Na_2O \cdot 2CaO \cdot 3SiO_2$. Addition of excess of any of the components, however, brings us into the ternary system, in which coexistence of these three phases produces not an invariant, but a monovariant system, and the temperature falls in each direction from *B*. On further addition of $CaO \cdot SiO_2$, the melting point continues to rise to the congruent melting of $Na_2O \cdot 2CaO \cdot 3SiO_2$, then falls to the eutectic between this compound and $CaO \cdot SiO_2$, then rises to the melting point of $CaO \cdot SiO_2$.

Of the two ternary compounds already considered, one has an incongruent, the other a congruent melting point. The one with a congruent melting point undergoes unusual dissociation in the liquid phase, as is shown by the shape of its melting point curve. A third ternary compound is met with in this system, of the composition $Na_2O \cdot 3CaO \cdot 6SiO_2$, and it is an extreme case of a compound with an incongruent melting point. The pure compound decomposes at 1060° into liquid and crystals of $CaO \cdot SiO_2$, and the melt does not become entirely liquid until 1325°. This complex compound is characterized by an extreme reluctance to crystallize, and every composition in which it is primary phase is a practical glass composition on a manufacturing scale. It is the primary crystallization from most commercial soda-lime-silica glasses, for which reason it has been named "devitrite."[14] Its field is shown in Figs. II. 6 and II. 7 by the area *NOPQR*, and on a larger scale in Fig. II. 8, which includes only compositions from 64 to 78 per cent SiO_2, 0 to 20 per cent CaO by weight.

The other fields in the diagrams require little discussion. The three forms of crystalline silica—cristobalite, tridymite and quartz—occupy

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[14] Morey, G. W., and Bowen, N. L., *Glass Ind.*, 12, 133 (1931).

fields the limits of which, as long as the boundaries are between forms of silica, are determined solely by the temperature. The region of immiscibility need not concern us here. The two sodium silicates occupy fields which run down to either one or the other of the ternary eutectics. $CaO \cdot SiO_2$ appears in two crystalline forms: α-$CaO \cdot SiO_2$, or pseudo-wollastonite, the high temperature form, and β-$CaO \cdot SiO_2$, the low temperature form, identical with the natural mineral wollastonite. The boundary between these forms is the line *ST*. The high temperature form frequently separates in the stability field of the low form, and, indeed, in the upper part of this field it is the more common. Also both forms frequently occur together at lower temperature, and once formed, the change from pseudo-wollastonite to wollastonite takes place very slowly indeed.

The sequence of phase and composition changes, beginning with the first formation of crystals at the liquidus to the final complete solidification to a conglomerate of crystalline phases, is called a crystallization path. Crystallization paths afford a clear insight into the meaning of phase equilibrium diagrams, and a number of typical ones will be discussed in detail.

Consider first a mixture in the area $Na_2O \cdot SiO_2$-*AKI*. Any composition within the area deposits $Na_2O \cdot SiO_2$ as primary phase; the liquid follows a crystallization path lying on the straight line joining the liquid composition with that of $Na_2O \cdot SiO_2$, until either the boundary *AK* or *IK* is reached. Here, either $2Na_2O \cdot CaO \cdot 3SiO_2$ or $Na_2O \cdot 2SiO_2$, respectively, appears, and the liquid follows the boundary curve down to the ternary eutectic at *K*, where it solidifies completely.

A composition within the area *ABLK* follows an equally simple course, depositing first $2Na_2O \cdot CaO \cdot 3SiO_2$, then, in all cases except those compositions lying within the small area between *L* and the line joining *K* with $2Na_2O \cdot CaO \cdot 3SiO$, depositing $Na_2O \cdot SiO_2$ as secondary phase. Within the small area mentioned, $NaO \cdot 2SiO$ is the second phase to separate; in both cases, the mixture crystallizes completely at the ternary eutectic *K*.

Crystallization of mixtures lying within the region where $Na_2O \cdot 2CaO \cdot 3SiO_2$ is the primary phase is usually a less simple matter. Consider first a composition within the triangle $Na_2O \cdot SiO_2$-$Na_2O \cdot 2SiO_2$-$2Na_2O \cdot CaO \cdot 3SiO_2$, bounded by the curve *BL* and the straight line joining *L* with $Na_2O \cdot 2CaO \cdot 3SiO_2$. The primary phase is $Na_2O \cdot 2CaO \cdot 3SiO_2$; the liquid follows a crystallization path passing through the composition of the primary phase and of the original mixture, until this path cuts the boundary curve *BL*. At this intersection $2Na_2O \cdot CaO \cdot 3SiO_2$ crystallizes; the liquid then follows the boundary curve, the reaction $Na_2O \cdot 2CaO \cdot 3SiO + \text{liquid} = 2Na_2O \cdot CaO \cdot 3SiO$ takes place, and the proportion of the former compound decreases, while that of the latter increases, until at *L*, where $Na_2O \cdot 2SiO_2$ appears, the compound $Na_2O \cdot 2CaO \cdot 3SiO_2$ has been decomposed entirely. The liquid then follows the boundary curve *LK*, finally solidifying completely at the ternary eutectic *K* to a mixture of $Na_2O \cdot SiO_2$, $Na_2O \cdot 2SiO_2$, and $2Na_2O \cdot CaO \cdot 3SiO_2$. If the composition lies within the same triangle, but to the right of the join *L*-$Na_2O \cdot 2CaO \cdot 3SiO_2$, the end products will be the same, but the secondary phase will be $Na_2O \cdot 2SiO_2$, on the boundary *ML*; at *L*, reaction takes place resulting in the formation of $2Na_2O \cdot CaO \cdot 3SiO_2$ and the disappearance of $Na_2O \cdot 2CaO \cdot 3SiO_2$.

Any mixture in the triangle $Na_2O \cdot 2CaO \cdot 3SiO_2$-$2Na_2O \cdot CaO \cdot 3SiO_2$-$Na_2 \cdot 2SiO_2$ will solidify completely to a mixture of the above phases and $Na_2O \cdot 2SiO_2$, but the crystallization path will differ according to the side of the line *L*-$Na_2O \cdot 2CaO \cdot 3SiO_2$, on which the original composition lies. If the point representing the composition of the glass is to the left of the above line, the secondary phase is $2Na_2O \cdot CaO \cdot 3SiO_2$, and the liquid follows the boundary *BL* until the point *L* is reached. Here the reaction $L + Na_2O \cdot 2CaO \cdot 3SiO_2 = 2Na_2O \cdot CaO \cdot 3SiO_2 + Na_2O \cdot 2SiO_2$ takes place until the mixture has solidified completely. If the original mixture lies to the right of the line *L*-$Na_2O \cdot 2CaO \cdot 3SiO_2$, the same three phases are finally formed, but $Na_2O \cdot 2SiO_2$ is the second crystalline phase to separate, and at *L* the liquid of composition *L* reacts with the primary phase to form $Na_2O \cdot 2SiO_2$ and $2Na_2O \cdot CaO \cdot 3SiO_2$.

Glasses whose compositions lie within the field of $Na_2O \cdot 2CaO \cdot 3SiO_2$, and also within the triangle $Na_2O \cdot 2SiO_2$-$Na_2O \cdot 2CaO \cdot 3SiO_2$-$Na_2O \cdot 3CaO \cdot 6SiO_2$, all solidify completely as a mixture of these three crystalline phases, but the crystallization paths differ according to whether the composition is to the right or left of the line *N*-$Na_2O \cdot 2CaO \cdot 3SiO_2$. If to the left of this line, the second phase to appear is $Na_2O \cdot 2SiO_2$, along the boundary *MN*, and the residual liquid follows the line *MN* to the reaction-point *N*. Here the reaction $Na_2O \cdot 2CaO \cdot 3SiO_2 + \text{liquid } N = Na_2O \cdot 2SiO_2 + Na_2O \cdot 3CaO \cdot 6SiO_2$ takes place, until the liquid has entirely disappeared. If the original composition is to the right of the above line, either $CaO \cdot SiO_2$ or $Na_2O \cdot 3CaO \cdot 6SiO_2$ is the secondary phase. If separation of $Na_2O \cdot 2CaO \cdot 3SiO_2$ results in the liquid composition being displaced in such a direction that the boundary *CSRN* is intersected between *C* and *S*, the high temperature form of $CaO \cdot SiO_2$ separates, and should invert at *S* to the low temperature form; and if intersection takes place between *S* and *R*, the low form should separate. In either case, at *R* the reaction $CaO \cdot SiO_2 + \text{liquid } R = Na_2O \cdot 2CaO \cdot 3SiO_2 + Na_2O \cdot 3CaO \cdot 6SiO_2$ takes place, but there must be some residual liquid remaining after all the $CaO \cdot SiO_2$ has disappeared, because by hypothesis the original composition is outside the triangle formed by the three solid phases. The system thus becomes monovariant, and the liquid follows the boundary curve *RN*, with simultaneous crystallization of $Na_2O \cdot 2CaO \cdot 3SiO_2$ and $Na_2O \cdot 3CaO \cdot 6SiO_2$. At *N*, $Na_2O \cdot 2SiO_2$ appears, and the system is invariant. Reaction will take place as before, until the liquid has disappeared and only the same three crystalline phases are left.

It was possible for the above mixtures to solidify completely at *N* because the original composition was inside the triangle $Na_2O \cdot 2SiO_2$-$Na_2O \cdot 2CaO \cdot 3SiO_2$-$Na_2O \cdot 3CaO \cdot 6SiO_2$, and the liquid was exhausted while some $Na_2O \cdot 2CaO \cdot 3SiO_2$ remained. If the original mixture was in the field of this compound, but to the right of the tie-line $Na_2O \cdot 2SiO_2$-$Na_2O \cdot 3CaO \cdot 6SiO_2$, the $Na_2O \cdot 2CaO \cdot 3SiO_2$ disappears first, leaving liquid of the composition *N*. Since one of the solid phases has disappeared, the system is now monovariant, and the liquid will follow the boundary *NO*, with simultaneous crystallization of $Na_2O \cdot 2SiO_2$ and $Na_2O \cdot 3CaO \cdot 6SiO_2$, until at the ternary eutectic quartz appears, and the liquid will solidify completely. If the original composition was to the right of the tie-line *N*-$Na_2 \cdot 2CaO \cdot 3SiO_2$, the first boundary intersected will be *CSRN*, and the liquid will follow this boundary to the same reaction-point *N*. The details along this boundary will be discussed subsequently.

Crystallization paths within the field of $Na_2O \cdot 2SiO_2$ are simple. If the boundary intersected after passing through the field of $NaO_2 \cdot 2SiO_2$ is between *N* and *L*, $Na_2O \cdot 2CaO \cdot 3SiO_2$ will be the secondary phase, and the liquid will follow the boundary to *L*, and at this reaction point $2Na_2O \cdot CaO \cdot 3SiO_2$ will appear. If the original composition was inside the triangle $Na_2O \cdot 2SiO_2$-$2Na_2O \cdot CaO \cdot 3SiO_2$-$Na_2O \cdot 2CaO \cdot 3SiO_2$, at *L* the reaction $Na_2O \cdot 2CaO \cdot 3SiO_2 + \text{liquid } L = 2Na_2O \cdot CaO \cdot 3SiO_2 + Na_2O \cdot 2SiO_2$ will take place, and the mixture will solidify completely to these three crystalline phases. But if the original composition is within the triangle $Na_2O \cdot 2SiO_2$-$Na_2O \cdot SiO_2$-$2Na_2O \cdot CaO \cdot 3SiO_2$, when the reaction takes place at *L*, $Na_2O \cdot 2CaO \cdot 3SiO_2$ will disappear, and the monovariant liquid will follow *LK*, to solidify completely at the eutectic *K*. If the secondary phase is $Na_2O \cdot SiO_2$, the boundary intersected by the crystallization path will be *IK*. If the original composition is in the triangle $Na_2O \cdot 2SiO_2$-$Na_2O \cdot 3CaO \cdot 6SiO_2$-$SiO_2$, the crystallization path will end at the eutectic *O*. If the boundary *MN* is intersected, $Na_2O \cdot 2CaO \cdot 3SiO_2$ will be the second phase to appear, but it will disappear by reaction at *N*; then the liquid will follow *NO* to the eutectic. If the boundary intersected is *FO*, quartz will appear, and at *O*, $Na_2O \cdot 3CaO \cdot 6SiO_2$.

Glasses in which $CaO \cdot SiO_2$ is primary phase may follow several crystallization paths, depending on the composition, but in all cases the reactions are complicated. Mixtures within the triangle $Na_2O \cdot 2CaO \cdot 3SiO_2$-$CaO \cdot SiO_2$-$Na_2O \cdot 3CaO \cdot 6SiO_2$ will solidify ultimately as a conglomerate of these three phases. If the boundary intersected by the crystallization path is *CSR*, initial crystallization of $CaO \cdot SiO_2$ is followed by secondary $Na_2O \cdot 2CaO \cdot 3SiO_2$, and the liquid will follow this boundary to the reaction-point *R*. The reaction at this point, $CaO \cdot SiO_2 + \text{liquid } R = Na_2O \cdot 2CaO \cdot 3SiO_2 + Na_2O \cdot 3CaO \cdot 6SiO_2$, continues until one of the reacting phases disappears. When the original composition is within the triangle assumed above, the liquid phase is the first to disappear, and the mixture solidifies. If the boundary intersected by the crystallization path is *RQ*, to the left of the prolongation of the tie-line $CaO \cdot SiO_2$-$Na_2O \cdot 3CaO \cdot 6SiO_2$, this boundary is followed to *R*, and the same reaction takes place as before.

If the original composition is within the triangle $CaO \cdot SiO_2$-SiO_2-$Na_2O \cdot 3CaO \cdot 6SiO_2$, but in the $CaO \cdot SiO_2$ field, a similar course of crystallization is followed, with tridymite taking the place of $Na_2O \cdot 2CaO \cdot 3SiO_2$. The invariant point *Q* is reached either by the path *RQ*, in which case $Na_2O \cdot 3CaO \cdot 6SiO_2$ is secondary phase, or by the path *DTQ*, in which case tridymite is secondary phase. In either case, at *Q* the reaction $CaO \cdot SiO_2 + \text{liquid } Q = Na_2O \cdot 3CaO \cdot 6SiO_2 + SiO_2$ proceeds until the liquid has all disappeared.

Every mixture within the triangle $Na_2O \cdot 2SiO_2$-$Na_2O \cdot 3CaO \cdot 6SiO_2$-$SiO_2$ crystallizes finally at the eutectic *O*, but different mixtures take different courses to reach that point. Those within the fields of $Na_2O \cdot 2SiO_2$ and $Na_2O \cdot 2CaO \cdot 3SiO_2$ have been discussed. Those within the $CaO \cdot SiO_2$ field take the same course, which has already been described, to either *R* or *Q*. But when the reaction at this point is complete, the $CaO \cdot SiO_2$ will have been resorbed, and some liquid will remain. The system thus becomes monovariant, and follows either *RNO* or *QPO* to the eutectic.

Glasses in the field of $Na_2O \cdot 3CaO \cdot 6SiO_2$ follow a crystallization path along a straight line passing through the compound and the original glass, until a boundary is intersected. If the boundary is *RN*, the second phase is $Na_2O \cdot 2CaO \cdot 3SiO_2$, which at *N* reacts to form $Na_2O \cdot 2SiO_2$, as described above, then follows *NO*, but if the boundary intersected is *NO*, $Na_2O \cdot 2SiO_2$ will crystallize from the melt. In any case, when the liquid follows *NO*, at the eutectic quartz appears, and these three phases crystallize simultaneously until solidification is complete. If the boundary intersected is *QP*, tridymite is the phase to appear, and at *P* it inverts to quartz. The liquid then follows *PO*, and solidifies at the eutectic.

All the possible crystallization paths have now been discussed, with the exception of those arising in one of the SiO_2 fields. Any such path will intersect either *DTQPO* or *FO*, but in either case the subsequent reactions along these boundary curves have been discussed. *EP* is the transition curve of tridymite to quartz, a constant temperature curve.

The preceding discussion has been predicated on equilibrium being attained in all reactions, but of course it is the failure to reach equilibrium that chiefly makes this system of interest, and glass a possibility. Although it is usually not easy to obtain the equilibrium condition, it does not follow that this diagram does not give information as to the crystallization which will take place. It will rarely be found that the first phase to appear is other than that corresponding to the field within which its composition lies. The only case in which there is a probability

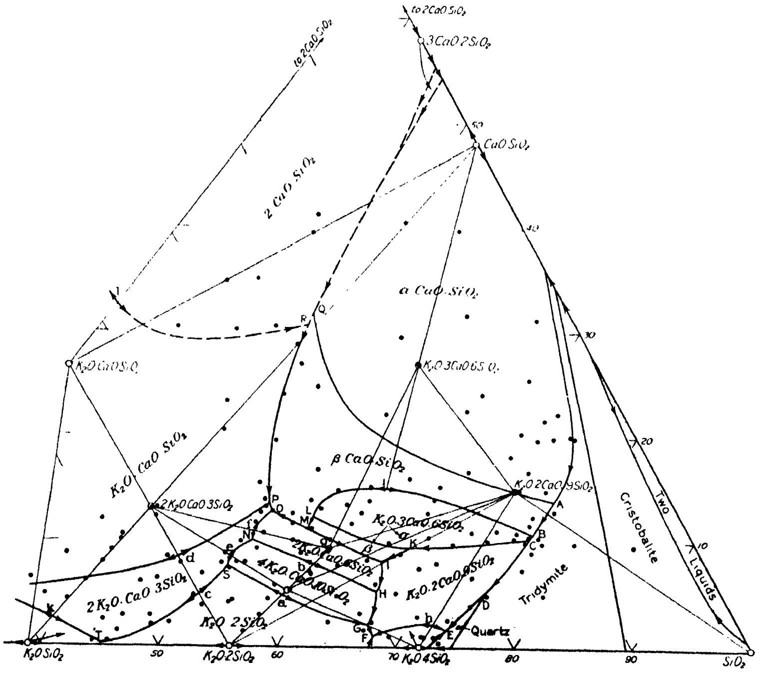

FIGURE II. 10.—Phase Equilibrium Diagram of the Ternary System K_2O-CaO-SiO_2. After Morey, Kracek and Bowen.

of this is in the $Na_2O \cdot 3CaO \cdot 6SiO_2$ field near the $CaO \cdot SiO_2$-$Na_2O \cdot 3CaO \cdot 6SiO_2$ boundary, especially near the tridymite invariant point. Here there is a possibility that either $CaO \cdot SiO_2$ or tridymite will come out as metastable phases when glass is cooling down; but such appearance of metastable phases is not to be expected on heating. The failure of the secondary crystallization to appear at a boundary within a given time has often been observed, but it will appear if time be given. The failure of a given phase to react to form another and stable phase, for example, of $CaO \cdot SiO_2$, to react to form $Na_2O \cdot 3CaO \cdot 6SiO_2$, or of tridymite to form quartz, has often been observed; but $CaO \cdot SiO_2$ has not been observed on heating a glass within the $Na_2O \cdot 3CaO \cdot 6SiO_2$ field, nor has the latter compound appeared in the quartz or tridymite field. Metastable crystallization is rarely met with in the $Na_2O \cdot 2CaO \cdot 3SiO_2$ or the $Na_2O \cdot SiO_2$ field. Cristobalite frequently separates in the field of tridymite.

The Ternary System K_2O-CaO-SiO_2

The ternary system K_2O-CaO-SiO_2[15] is more complicated than Na_2O-CaO-SiO_2, but the various features will be evident from Fig. II. 10 and Tables II. 1 and 2. The dissimilarity between the two systems is perhaps more marked than the similarity. In the system containing potassium oxide the field of the double orthosilicate of potassium and calcium spreads over the metasilicate join, and the analog of the compound $Na_2O \cdot 2CaO \cdot 3SiO_2$ is lacking. The compound $K_2O \cdot 3CaO \cdot 6SiO_2$, analogous to the compound "devitrite," occurs in two modifications, each of which is stable in contact with liquid. There are, moreover, compounds formed in the potassium system which have no analog in the sodium system, namely, two disilicates, $4K_2O \cdot CaO \cdot 10SiO_2$ and $2K_2O \cdot CaO \cdot 6SiO_2$, and the trisilicate $K_2O \cdot 2CaO \cdot 9SiO_2$. The system is characterized by the formation of more compounds than the system Na_2O-CaO-SiO_2, by the tendency of these compounds to dissociate on melting, by the greater viscosity of the melts at the liquidus over a large portion of the diagram, and by the great sluggishness of the crystallizing and melting process in portions of the diagram.

System K_2O-PbO-SiO_2

The ternary System K_2O-PbO-SiO_2 was worked out by Geller and Bunting.[16] Five ternary compounds were identified optically in the system, and the compositions of four of these established. These four have the compositions $K_2O \cdot 2PbO \cdot 2SiO_2$, $K_2O \cdot 4PbO \cdot 8SiO_2$, $K_2O \cdot PbO \cdot 4SiO_2$, and $2K_2O \cdot PbO \cdot 3SiO_2$; their properties are given in Table II. 1. The crystalline phase of undetermined composition apparently melts incongruently at about 750° to form glass and SiO_2. The crystals are platy, the indices $\alpha = 1.64$, $\beta = 1.65$, $\gamma = 1.655$, 2V about 80°, character biaxial negative.

Glasses in that portion of the ternary diagram (II. 11) on the silica side of the tie-lines connecting the compositions $K_2O \cdot 4SiO_2$, $K_2O \cdot PbO \cdot 4SiO_2$, $K_2O \cdot 4PbO \cdot 8SiO_2$ and $PbO \cdot SiO_2$ are stable in air. Compositions within this area and near these tie-lines fuse to homogeneous glasses with sufficient ease to be of possible commercial application, and all the potash flint glasses of commerce lie within this area. However, the tem-

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[15] Morey, G. W., Kracek, F. C., and Bowen, N. L., *J. Soc. Glass Tech.*, **14**, 149 (1930); **15**, 57 (1931).

[16] Geller, R. F., and Bunting, E. N., *J. Research Natl. Bur. Standards*, **17**, 277 (1936).

peratures required to produce a glass, and the viscosity of the product, rise very rapidly with increase in silica. Compositions on the K_2O-side of the tie-lines mentioned are either unstable in air, or, in that area bounded by the tie-lines from $PbO \cdot SiO_2$ to $K_2O \cdot 2PbO \cdot 2SiO_2$ are prone to devitrification.

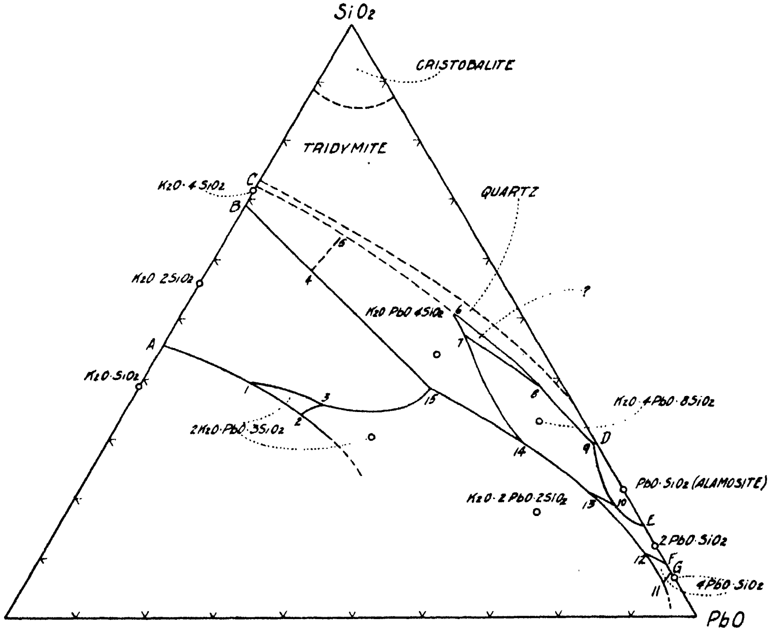

FIGURE II. 11.—Phase Equilibrium Diagram of the Ternary System K_2O-PbO-SiO_2. After Geller and Bunting.

Multi-Component Glasses

Complete phase equilibrium studies on mixtures more complex than ternary have not been made. Some partial studies[17] have been made on mixtures containing four components, and of these the only ones having a direct application to glass technology have dealt with the effect of small quantities of alumina, magnesia, and boric oxide on the devitrification of soda-lime glasses.

The effect of magnesia is of especial importance because of the frequent use of dolomitic limestone in glass manufacture. The complete solution of this problem would require a knowledge of the phase equilibrium in the quaternary system. The only study is that of Morey,[18] who made two series of experiments, representing two limited excursions

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[17] Morey, G. W., *J. Soc. Glass Tech.*, **20**, 245 (1936).

[18] Morey, G. W., *J. Am. Ceram. Soc.*, **13**, 714 (1930).

into the quaternary system Na_2O-MgO-CaO-SiO_2, both starting from the same point in the ternary system Na_2O-CaO-SiO_2, and proceeding in arbitrary directions. In both cases the parent glass had the percentage composition: Na_2O, 14.86; CaO, 9.83; SiO_2, 75.25, corresponding to the molecular ratios 1.15 Na_2O:0.84 CaO:6SiO_2. In one series, CaO was replaced by MgO, with the final glass having a composition near $Na_2O \cdot MgO \cdot 6SiO_2$. In the other series, MgO was added to the same parent glass, the composition tracing a straight line through the solid tetrahedral model representing the four-component system from the given point on one side toward the MgO-apex.

The results of the experiments are given in Fig. II. 12. The contrast between the two curves is striking. The parent glass is in the tridymite field. Curve I refers to the glasses obtained by replacing CaO by MgO, and it is evident that the melting point is lowered and the glass remains in the tridymite field. Curve II refers to the addition of MgO to the parent glass. Addition of 2.4 per cent MgO changed the primary phase from tridymite to the compound $Na_2O \cdot 3CaO \cdot 6SiO_2$, and the melting point was lowered almost 200°. On this arbitrary line

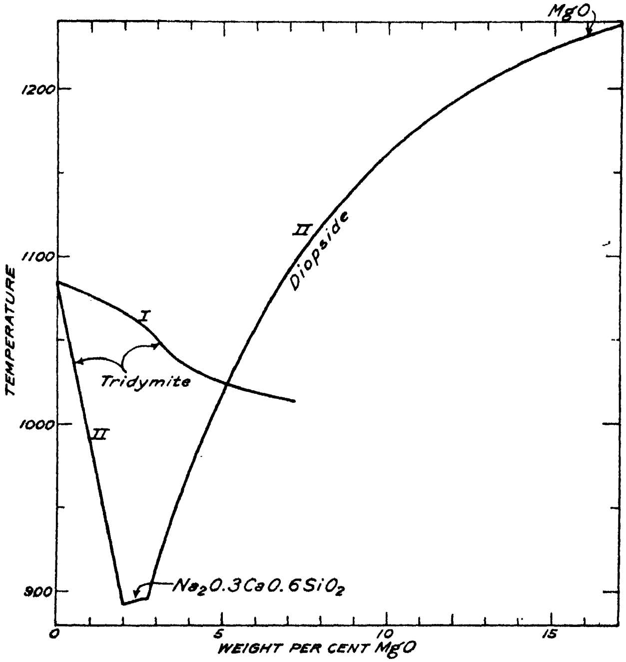

FIGURE II. 12.—Effect of Magnesia on the Liquidus Temperatures of Some Glasses in the System Na_2O-CaO-SiO_2. After Morey.

through the tetrahedron, the compound $Na_2O \cdot 3CaO \cdot 6SiO_2$ has a very narrow field, but it is probable that further experimentation would find mixtures in which its field would extend further into the ternary diagram, with benefit both to the ease of melting and to thermal stability. On continued addition of MgO, the mineral diopside ($CaO \cdot MgO \cdot 2SiO_2$) was formed and remained the stable phase far into the quaternary system. Diopside crystallizes readily from these melts, and glasses much within its field would not prove suitable for manufacture on a large scale.

That the presence of alumina greatly diminished the tendency of a soda-lime glass to devitrify has been known since Schott[19] showed that the superiority for table and blowpipe working of certain glasses made in the Thuringian Forest was caused by the presence of about 4 per cent alumina in the sand used, and that addition of alumina to the usual glass batches greatly reduced the tendency toward devitrification of the resulting product. The observations of Schott, confirmed as a matter of common experience by many workers with glass, had to do with the velocity of devitrification under conditions which were not only variable but also practically undefined. To correlate these observations with the

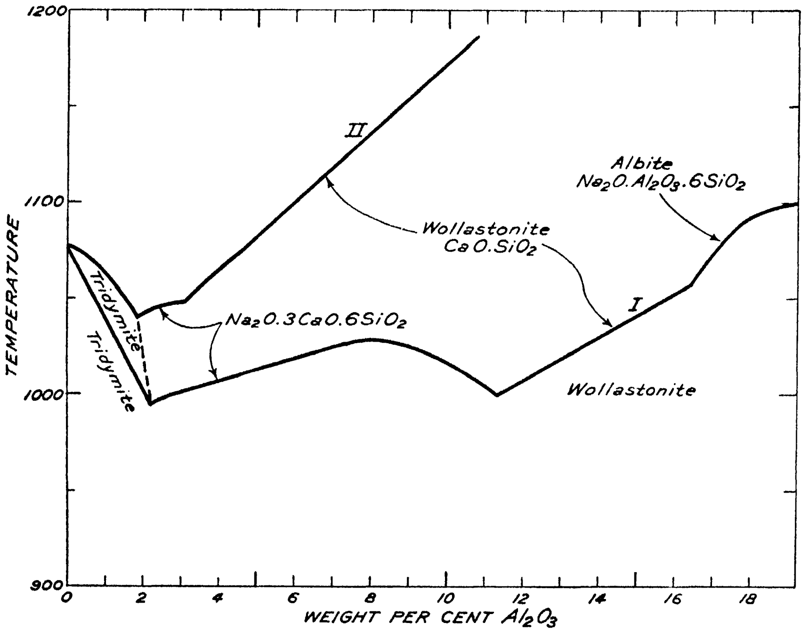

FIGURE II. 13.—Effect of Alumina on the Liquidus Temperatures of Some Glasses in the System Na_2O-CaO-SiO_2. After Morey.

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[19] Schott, O., "Verhandl. Ver. Beförd. Gewerbefleisses," 799 (1887).

effect of alumina on the temperature of initial devitrification of glass was one reason for the experiments of Morey,[20] the only study of the four-component system Na_2O-Al_2O_3-CaO-SiO_2 which has been published.

The plan of the experiments was similar to that of the effect of magnesia, already discussed. The parent glass had the percentage composition: Na_2O, 14.3; CaO, 11.0; SiO_2, 74.7, corresponding to the molecular ratio 1.11 Na_2O:0.95 CaO:6SiO_2, and was in the tridymite field. The results of the experiments are shown by the curves of Fig. II. 13. On replacing CaO by Al_2O_3 (Curve I) there was a sharp drop in the liquidus temperature, about 80° for 2 per cent Al_2O_3, and the glass crossed the tridymite field and entered that of $Na_2O \cdot 3CaO \cdot 6SiO_2$. The liquid then crossed the fields of $Na_2O \cdot 3CaO \cdot 6SiO_2$, of wollastonite ($CaO \cdot SiO_2$), and finally entered the field of albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$), the end-point of this series of experiments. When Al_2O_3 was added to the same glass (Curve II), the lowering of the melting point was not so great, the field of $Na_2O \cdot 3CaO \cdot 6SiO_2$ was narrower, and $CaO \cdot SiO_2$ remained primary phase as far as the curve was followed, up to 9.1 per cent Al_2O_3 and 1156°, at which point the temperature was increasing rapidly.

These experiments, as well as the ones with MgO discussed above, were merely linear excursions into the quaternary system, and it is evident that no generalizations can be made. Only by experiment can the facts in regard to solubility and fusion relations be determined, and generalizations from insufficient data are sure to lead to erroneous conclusions.

A more extensive study of a four-component system is that by Morey[21] on the effect of boric oxide. Twenty-one parent glasses were used, in or near the field of $Na_2O \cdot 3CaO \cdot 6SiO_2$, and boric oxide was added in amounts sufficient to cause a change in the initial crystallization. One effect of boric oxide was to shift the position of the boundary curves, as is shown by Fig. II. 14, on comparison with Fig. II. 7. The field of $Na_2O \cdot 3CaO \cdot 6SiO_2$ is shifted away from the SiO_2-apex, more on the side adjoining the field of $Na_2O \cdot 2CaO \cdot 3SiO_2$ than on that adjoining tridymite.

The initial effect of addition of B_2O_3 depends on the composition of the parent glass. When it is in the tridymite field, the initial depression of the liquidus ranges from about 10° to 15° per 1 per cent B_2O_3; but on further addition of B_2O_3 the liquidus may rise to a maximum. The initial depression, followed by elevation, of the liquidus, was observed with glasses containing 10 per cent B_2O_3, and the liquidus was continuously depressed in the glasses containing 7.5 per cent CaO. Glasses in the wollastonite field show an initial freezing point lowering of from

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[20] Morey, G. W., *J. Am. Ceram. Soc.*, **13**, 718 (1930).

[21] Morey, G. W., *J. Am. Ceram. Soc.*, **15**, 457 (1932).

15° to 25° for 1 per cent B_2O_3. When near the boundary between the wollastonite and tridymite fields, they pass into the latter, and the liquidus temperature goes up, probably to fall again. When the original glass is farther from the tridymite boundary, addition of B_2O_3 brings it into the field of $Na_2O \cdot 3CaO \cdot 6SiO_2$, and the lowering continues. Glasses in the field of $Na_2O \cdot 3CaO \cdot 6SiO_2$ show an initial lowering of about the

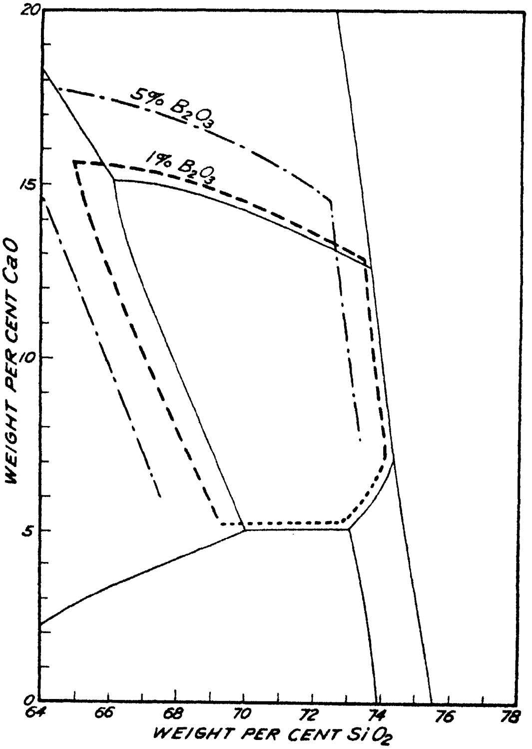

FIGURE II. 14.—Effect of Boric Oxide on the Field of Devitrite, $Na_2O \cdot 3CaO \cdot 6SiO_2$, in the System Na_2O-CaO-SiO_2. After Morey.

same amount. When they are near the tridymite field, the boundary is soon passed, and the liquidus may either continue to fall, or may rise to a maximum, before falling. Glasses in the field of $Na_2O \cdot 2CaO \cdot 3SiO_2$ show the largest initial lowering, amounting to from 40° to 60° for 1 per cent B_2O_3 added.

In some respects, the effects of addition of B_2O_3 are those to be expected from its being an oxide capable of entering into combination with Na_2O and CaO, in competition with SiO_2, but such a hypothesis fails to account for all the facts. The process assumed probably plays a part, but other and specific effects of B_2O_3 make any generalization unsafe.

The preceding discussion has dealt with experimental glasses, although some of the compositions are essentially the same as some commercial glasses. Morey[22] also made a study of the devitrification of three types of "Pyrex" resistant glasses, known by the factory designations of 774 ($n = 1.471$), 772 ($n = 1.485$) and 776 ($n = 1.473$). The first of these is the type of glass widely used for the manufacture of beakers, flasks and other chemical ware, the usual composition of which is given in Table III. 3, No. 20. The liquidus temperatures found were: 772, 1042°; 774, 1077°; 776, 1036°. "Pyrex" glass 774 has the lowest liquidus temperature of any known mixture having so high a silica content, and in this fact doubtless is to be found a clue to its exceptional ability to withstand devitrification.

The liquidus temperature of a glass indicates the limit above which devitrification cannot take place, and below which there is a possibility of devitrification. Glasses are commonly exposed for not inconsiderable periods to temperatures below their liquidus, and the composition must be such that, in spite of the favorable conditions, devitrification does not take place. The generalization may be made that, other factors being equal, the lower the liquidus and the higher the silica content, the less will be the danger of devitrification.

The Effect of Inhomogeneities

In carrying out the phase equilibrium studies, the greatest care must be exercised to make sure that the preparations are homogeneous. This usually requires that the glasses be repeatedly powdered and remelted. It is not sufficient to assume homogeneity; that the glasses are homogeneous should be proved. This is best done by examining the powder under a microscope, when the powder is immersed in a liquid closely matching it in refractive index. If the index of the liquid is a little higher than that of the glass, it can be made less than that of the glass by warming, and during cooling to ordinary temperature it will exactly match the index of the glass. Under these conditions a very small variation in composition can be detected by its effect on the refractive index of the glass.

The quenching technique offers a powerful method of detecting an inhomogeneity. When a homogeneous glass is held a little below the liquidus, so that there is present only a small amount of crystalline material, the distribution of that material is significant. The powdered quench is examined under a microscope, and usually several hundred grains will be examined. If the crystals are uniformly distributed, the

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[22] Morey, G. W., *J. Am. Ceram. Soc.*, **14**, **529** (1931).

glass may be assumed to be homogeneous. But if the distribution is not uniform, if many grains contain no crystals, while others are crowded with them, it is positive evidence that the original glass is not of uniform composition, and steps must be taken to correct this fault. Stirring of small melts is usually futile, at least with most silicates. Repeated grindings and meltings have been found to be the surest way to prepare satisfactory glasses on a small scale.

Industrial glasses are rarely homogeneous, and this fact must be taken into account in determining the liquidus temperature of such glasses. The fault lies in the glasses; if the material on which measurements of any kind are made is not of determinable and known composition, the value of the measurements is greatly diminished. Gross inhomogeneity in a commercial glass will often result in trouble from devitrification when a homogeneous glass of the same total composition would be satisfactory. Liquidus measurements on such glasses are in themselves meaningless, since they represent the crystallization from regions of unknown composition; but the information to be gained in the course of such measurements as to the departure of the glass from uniformity is helpful in itself, and is salutary in emphasizing the effects of the heterogeneity. Improvement of commercial glasses in this respect will probably be an important development in the near future, and the result of that improvement will be reflected in most of the properties of the product.

Studies on Devitrification and Its Rate

Several other studies of the devitrification of soda-lime-silica glass have been made. Schaller [23] gave two graphs showing "upper devitrification temperature" as a function of composition, but no details of procedure. One graph refers to Na_2O-CaO-SiO_2 mixtures, and roughly agrees in shape with the liquidus curve of that system as determined by Morey and Bowen, but the temperatures are from 50° to 100° lower. A curve is given showing the "temperatures of devitrification," presumably meaning the upper limit, which should be identical with the liquidus temperature; the agreement with the results of Morey and Bowen is not good.

Gelstharp and Parkinson [24] divided the ternary system into several fields by the application of various criteria which render the successive composition regions unsuitable for use as glass, until they excluded all regions except a part near to, and including, the boundary between the fields of tridymite on the one side, and $CaO \cdot SiO_2$ and $Na_2O \cdot 3CaO \cdot 6SiO_2$ on the other.

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[23] Schaller, R., *Z. angew. Chem.*, **22**, 2369 (1909).

[24] Gelstharp, F., and Parkinson, J. C., *Trans. Am. Ceram. Soc.*, **16**, 109 (1914).

Zschimmer and Dietzel[25] made a study of the devitrification of a technical soda-lime glass, and Dietzel[26] studied the rate of devitrification of a number of soda-lime glasses, as a function of temperature. The method was to heat the glass for suitable periods, measure the length of the crystals produced in the given time, and calculate the crystallization velocity in 0.001 mm. per minute. The usual time was about ten minutes. An example of the curves so obtained is given in Fig. II. 15.

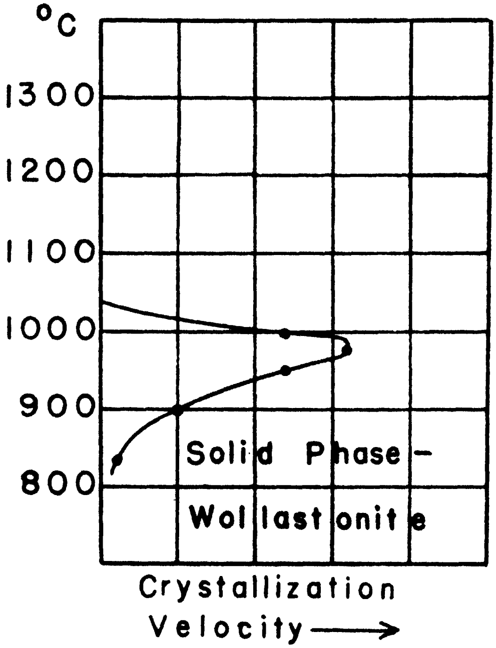

FIGURE II. 15.—Velocity of Crystallization of a Glass of the Percentage Composition: SiO_2, 69.93; Na_2O, 15.96; CaO, 13.97; Al_2O_3, etc., 0.14. After Dietzel.

The maximum crystallization velocity is dependent on the composition of the glass, and the results are summarized in Fig. II. 16, reproduced from Dietzel. The curves show the compositions having maximum velocity at the same temperature. There is a sharp curvature not far from the boundary between the fields of tridymite, on one side, and $Na_2O \cdot 3CaO \cdot 6SiO_2$ and $CaO \cdot SiO_2$, on the other, indicated by line A-A on the diagram. It is concluded that for maximum freedom from devitrification the glass should contain 74 per cent SiO_2.

The extrapolation of the curves giving the velocity of devitrification to their upper limit at the intersection with the vertical axis should

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[25] Zschimmer, E., and Dietzel, A., *Sprechsaal*, **60**, 110, 129, 165, 186, 204 (1927).

[26] Dietzel, A., *Sprechsaal*, **62**, 506, 524, 543, 562, 584, 603, 619, 638, 657 (1929).

give the liquidus temperature, and on the whole there is good agreement with the results of Morey and Bowen. The best agreement is where extrapolation was shortest, which is where crystallization takes place quickly.

Parmelee and Monack[27] determined the relative stabilities of several glasses by a "thermal treatment" which consisted of "heating them in small crucibles until they were fluid, and then slowly cooling them so that a period of 12 to 15 hours was required to reach room temperature."

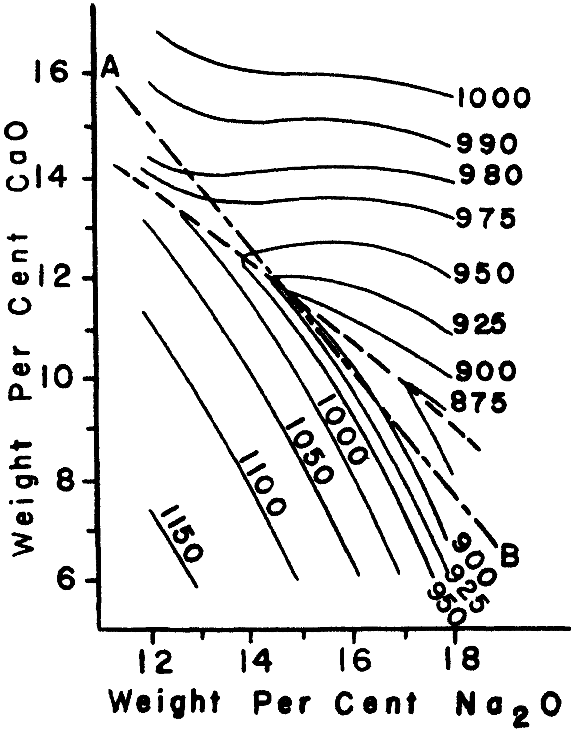

FIGURE II. 16.—Isotherms of Maximum Velocity of Crystallization in the System Na_2O-CaO-SiO_2. After Dietzel. The Line AB is the Boundary between the Fields of Devitrite and Tridymite, according to Morey and Bowen.

They also determined a time-temperature rate of devitrification curve for some glasses by heating samples at constant temperature for increasing periods until crystallization was found to have begun. The times required at various temperatures were assembled in curves, which should give valuable information as to the tendency of the glass to devitrify, when the determinations are made with a knowledge of the liquidus

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[27] Parmelee, C. W., and Monack, A. J., *J. Soc. Glass Tech.*, **13**, 322 (1929).

temperature of the glass. The region of acceptable glass compositions so defined agrees well with that deduced from the phase equilibrium results.

Peddle[28] studied the devitrification of numerous series of glasses of differing composition, as a part of his valuable contribution to the science of glass. In general, he heated small pieces in a muffle at 900° for six hours, then cooled them in twelve hours. The results indicate only that the glasses do or do not devitrify under the given condition. In some cases the temperature chosen was above the liquidus. There is, of course, no way to distinguish the effects taking place at 900° from those taking place during cooling.

Arthur[29] discussed the chemical composition of window glass on the basis of the equilibrium diagram determined by Morey and Bowen.

Measurements of the rate of devitrification require great care in specifying the conditions and history of the glass if the results are to be of value. As great care should be taken to obtain homogeneous glasses as is required in liquidus determinations; otherwise the results can be of little significance. Aside from the experimental difficulties there are serious theoretical difficulties.

Rates of reaction in general are very susceptible to alterations in experimental conditions, often of factors unknown and difficult to specify. Below the liquidus the uncrystallized condition is unstable, but to transform it into the stable mixture of glass and crystal may be difficult. It is not known what factors determine the velocity with which the unstable glass becomes transformed into the heterogeneous assemblage which is stable at the temperature in question. The difference in energy content, more exactly, the difference in the value of the zeta-function defined by Gibbs,[30] frequently called the "free energy," is the source of the driving force of the reaction. However, it is well known that the velocity of chemical reactions in general bears no simple relation to the change in free energy in the reaction. The identification of the various opposing resistances which prevent the immediate attainment of the equilibrium condition, and the assigning to each of these its appropriate weight, is not possible with our present knowledge of the processes operative in solutions, but it seems probable that viscosity plays an important, perhaps a dominant, role. Since both the driving force and the opposing resistance offered by viscosity increase with decreasing temperature, and the force is zero at the liquidus, it necessarily follows that there will be an optimum temperature for crystallization. Reinders,[31] on the basis of similar reasoning, has obtained an equation connecting the liquidus temperature and the temperature of

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[28] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 34 (1920).

[29] Arthur, E. P., *J. Am. Ceram. Soc.*, **9**, 203 (1926).

[30] "The Scientific Papers of J. Willard Gibbs," **1**, 87, eq. 91, Longmans, Green, New York, 1906.

[31] Reinders, W., *Rec. trav. chim.*, **51**, 589 (1932).

maximum crystallization velocity which reproduces the observed type of curve. But that is no proof that the viscosity is the dominant factor.

The measurements which have been made do not necessarily afford an adequate measure of the velocity of crystallization under the conditions of the experiment. The time is taken as that during which the sample is exposed to the furnace temperature, and takes no account of the part of that time required for the crystallization process to begin. The difference is not significant with mixtures which crystallize in a few minutes, but it is significant with mixtures hard to crystallize. For example, potassium silicates which require a month or so to crystallize may be left in the furnace for two weeks without apparent effect, even when examined under a microscope. But some change has taken place; because the glass so treated will now crystallize much sooner than one which has not had the heat treatment. Glasses exceptionally hard to crystallize, near the alkaline feldspars in composition, crystallize more readily if they are cooled slowly from the melting to the crystallizing temperature, and then held until crystallization begins, than if they are first cooled quickly to room temperature, and then heated to the crystallizing temperature. There must be some changes in the internal equilibrium of the melt which take place slowly at the crystallizing temperature, with the correspondingly high viscosity, but more rapidly at higher temperature when the melt is less viscous; and these changes in internal equilibrium are necessary preliminaries to crystallization.

While we have no information as to the nature, composition, and persistence of the "molecular aggregations" (using the term in a deliberately vague sense as indicating some unknown factor in the constitution of the liquid) present in a glass at its liquidus temperature, the fact that many of the compounds formed on crystallizing are highly dissociated, and hence for their formation require a considerable diffusion of matter, must be an important factor. The compound which crystallizes from a melt may not be, and probably is not, that which is present in the glass in largest amount. The compound which separates is that which first becomes insoluble in the melt, and its crystallization requires a continuous shifting of the proportions of the other molecular species. The time required for the formation of the first traces of crystals should not be included in that used in calculating the velocity of crystallization, although when the total time is short it may make no detectable difference.

It is not probable that surface energy plays an important part in the devitrification process; and whatever role it may play is not determined by the quantity usually measured, the surface tension at the interface glass-air, but by that at the interface between glass and crystal at the temperature in question, a quantity which never has been measured. This quantity will affect the amount of undercooling necessary to form the surface of an infinitesimally small nucleus, but once such a nucleus is formed the importance of the surface energy will not be significant.

It is frequently stated that glass devitrifies more readily on the surface, and that when devitrification takes place the initial growth takes place from the surface. This probably is true under the conditions to which the experiments relate, but it is not true in general. Morey[32] states that during the course of many experiments special care was taken to observe the manner of growth of the crystals, and in no case have the crystals grown from a surface, and in no case has there been observed crystals growing from the surface of discontinuity of bubbles. It appears that the explanation of the effect must be sought in some cause other than the effect of the surface itself. Sometimes the surface of an article contains inhomogeneities or even small crystals carried over from the surface of the melt in the pot or tank, which may affect subsequent devitrification. In the case of materials which have been fire-polished, a difference in surface composition, caused by loss of alkali or boric oxide, may be the explanation. The obvious fact that the surface first reaches the optimum temperature for crystallization may frequently be the whole cause.

When a fresh surface of glass is formed, the instantaneous value of the surface tension will be that of material of composition uniform with the glass in mass; but, since the energy of a complex system is a function not only of temperature and surface but also of composition, there will begin at once a concentration at the surface of those components whose influence is to lower surface tension. Whether the surface in this altered state will have a lower or higher liquidus temperature than in the unaltered condition it is not possible to state in general, because this is determined entirely by the specific properties of the particular composition, but in any case there is no parallelism between this effect and surface tension. It has also been stated that the excess energy inherent in the surface will cause crystallization to take place more readily than in the interior of the mass, because of a consequent greater mobility of the atoms forming the surface. This reasoning is fallacious. The excess energy is potential, not kinetic. Moreover, if we make that assumption in regard to glass which has been demonstrated experimentally in the case of numerous other liquids, namely, that the surface molecules or molecular groupings are oriented, and in general in such a manner that the long axis of such groupings is normal to the surface, it is probable that those units of structure comprising the surface are subject to constraint which limits their movements, and may even diminish their degree of freedom. To describe the devitrification of glass as a surface phenomenon is misleading.

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[32] Morey, G. W., *J. Am. Ceram. Soc.*, 13, 683 (1930).

Chapter III

The Composition of Glass

All known glasses are undercooled liquids, and that property which makes possible their manufacture and working, namely, the property of remaining in the liquid condition while passing through the temperature range immediately below the freezing point and persisting in that condition indefinitely at ordinary temperatures, is the most important and characteristic property of glass. This property is possessed by many substances in widely differing degrees. Some silicate glasses, for example, those formed by fusing the alkali feldspars, are practically impossible to crystallize by heat treatment alone, that is, without the aid of "mineralizers." Some silicates, for example, sodium metasilicate, can be obtained as glass by rapidly cooling a melt of a few grams or less, but larger melts cannot be cooled without devitrification. Other silicates, and some other compounds, can be obtained as glass only by chilling them with the greatest possible rapidity, for example, by dropping a melt of only a few milligrams into mercury, or by spraying the liquid on a cold surface. Many, possibly most, compounds cannot be obtained as glass by the most rapid cooling possible.

Some elements can be obtained in the glassy form, notably selenium and tellurium. Amorphous sulfur is too fluid at ordinary temperature to be considered as glass, but glassy mixtures of it with selenium have been used.[1] Selenium also forms glassy mixtures with phosphorus.[2]

A number of inorganic salts have been obtained as glass, notable among which is beryllium fluoride. Complex glasses have been prepared[3] containing it together with one or more of the fluorides of potassium, sodium, lithium, calcium, magnesium and aluminum. Zinc chloride[4] when quickly cooled forms a glass, which gradually crystallizes after standing some weeks or months in air, probably as the result of having taken up moisture. The nitrates of potassium, sodium, and silver, thallous sulfate, and lead chloride[5] have been obtained as tiny glassy droplets by spraying the molten material onto a cold plate. The double carbonate, $K_2Mg(CO_3)_2$, which must be melted under pressure,

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[1] Merwin, H. E., and Larsen, E. S., *Am. J. Sci.*, **34**, 42 (1912).

[2] Robinson, P. L., and Scott, W. E., *Z. anorg. allgem. Chem.*, **210**, 57 (1933).

[3] Heyne, *G.*, *Angew. Chem.*, **46**, 473 (1933).

[4] Maier, C. G., *Tech. Paper 360, U. S. Bureau of Mines*, 1925.

[5] Tammann, G., and Elbrächter, A., *Z. anorg. allgem. Chem.*, **207**, 268 (1932).

normally cools to a glass.[6] Sodium thiosulfate, "hypo," alums and some other hydrated salts form glass on rapid cooling.

Water is a possible constituent of glass. The complex glasses obtained by evaporating aqueous solutions [7] usually contain water. Many natural glasses contain water, sometimes as much as 11 per cent. Morey and Fenner [8] prepared a series of glasses containing water by fusion of potassium silicates with water under pressure. They were typically hard and brittle when the water content was less than 10 per cent, and with increasing amounts of water became first stiff jellies, then obviously viscous liquids.

Most glasses may be regarded as composed of oxides, and the possibility of glass formation may be intimately connected with the oxygen atoms. Oxygen itself is highly viscous at its melting point, and it is not improbable that it could be obtained as glass by proper manipulation. The outstanding glass-forming oxides are: boric oxide, B_2O_3, silica, SiO_2, and phosphorus pentoxide, P_2O_5. Germanium oxide, GeO_2, is an excellent glass-former; and if it were not so expensive, it might have commercial use. Vanadium pentoxide, V_2O_5, forms a glass, and some vanadates can be obtained in the glassy condition. Arsenious oxide, As_2O_3, forms a glass, and some of the As_2O_3 in the market is called "vitreous," although it usually has devitrified by the time of purchase.

A large number of substances and mixtures can be obtained as glasses by proper manipulation, but only a comparatively few compositions are suitable for glass manufacture on a commercial scale. All such contain a large proportion of the glass-forming oxides mentioned above. Of these, phosphoric oxide is little used, because its glass-forming properties are not as marked as those of the other two, and because glasses containing a large amount of it are susceptible to attack by water or by weak acids. Boric acid is used extensively, but only as a constituent of silicate glasses, because when used without silica or in too large a proportion, the resulting glasses lack chemical durability. Commercial glasses are almost exclusively silicate glasses, and the natural glasses are all silicates. Because the natural glasses differ in composition from artificial glasses, they will be considered separately.

Natural Glasses

Natural glasses (Table III. 1) may be divided into two groups: those which are of igneous origin, representing magmas which have been cooled quickly enough to prevent crystallization; and the fulgurites and tektites.

Fulgurites are formed by lightning striking sand, or other loose or porous material. Before Franklin discovered the true explanation of

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[6] Skaliks, W., *Schriften königsberg. gelehrten Ges.*, **5**, 93 (1928).

[7] Balke, C. W., and Smith, E. F., *J. Am. Chem. Soc.*, **25**, 1229 (1903).

[8] Morey, G. W., and Fenner, C. N., *J. Am. Chem. Soc.*, **39**, 1173 (1917).

TABLE III. 1—Compositions of Some Natural Glasses

No.	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O+	H_2O-	TiO_2
1	97.58	1.54	...	0.23	...	0.38	0.34		0.10		
2	87.00	8.00	0.19	1.93	0.82	nil	0.14	0.99	0.36		0.51
3	76.89	12.72	0.43	0.70	0.17	0.57	3.48	4.39	0.47	0.02	0.08
4	76.37	12.59	0.26	0.48	0.17	0.79	3.36	4.67	0.97		0.11
5	74.70	13.72	1.01	0.62	0.14	0.78	3.90	4.02	0.62	...	...
6	73.92	12.38	1.62	0.56	0.27	0.33	3.49	5.39	1.69		
7	71.60	12.44	1.00	0.65	0.06	1.90	3.30	4.22	3.78	0.81	0.25
8	70.62	11.54	1.20	0.18	0.26	1.72	3.52	1.45	7.24	2.42	0.04
9	70.56	20.54		0.96	0.11	0.78	3.47	3.38			
10	69.95	11.99	0.76	0.64	0.09	0.66	3.70	3.80	4.98	2.80	0.18
11	68.12	12.13	n.d.	1.03	tr.	1.63	5.34	1.69	9.70		
12	67.55	15.68	0.98	1.02	1.11	2.51	4.15	2.86	2.76	0.38	0.34
13	66.68	13.39	0.91	0.21	none	2.72	2.23	2.51	10.05		0.38
14	61.4		5.8		2.9	10.3	2.4	10.1			
15	60.12	17.67	3.75	3.40	0.53	2.40	6.78	4.43	0.49		
16	58.59	21.29	4.74	0.71	2.49	6.36	4.42	0.94	0.27	0.04	
17	53.10	20.70	0.07	4.77	1.77	3.18	9.10	5.84	0.70		0.47
18	50.76	14.75	2.89	9.85	6.54	11.05	2.70	0.88	n.d.		

1. Fulgurite from Libyan desert. Clayton, P. A., and Spencer, L. J., *Mineral. Mag.*, **23**, 501 (1934).
2. Darwin glass, Tasmania. David, T. W. E., Summers, H. S., and Ampt, G. A., *Proc. Roy. Soc. (Victoria)*, **39**, 157 (1927).
3. Obsidian, New Zealand. From the compilation, "The Chemical Analyses of Igneous Rocks," Washington, H. S., U. S. Geological Survey, Prof. Paper No. 14 (1917). (Subsequently referred to as HSW.) 72, Analysis No. 100.
4. Columbite, Tetilla, near Papayan. Döring, Th., and Stutzer, O., *Centr. Min.*, Abt. A, 35 (1928). Also contains MnO, 0.14; SO_3, 0.13; Sb_2O_3, 0.07; P_2O_5, 0.02.
5. Obsidian, Obsidian Cliffs, Yellowstone National Park. HSW, 62, Analysis No. 18. Also contains FeS_2, 0.40.
6. Obsidian, Cerro de los Navajo, Tulancingo, Mexico. HSW, 126, Analysis No. 105. Also contains P_2O_5, 0.27.
7. Rhyolite glass, Burton Peak, Nevada. HSW, 186, Analysis No. 155. Also contains P_2O_5, 0.08; MnO, 0.06; ZrO_2, 0.01; BaO, 0.05; SrO, 0.03.
8. Rhyolite glass, New South Wales. HSW, 96, Analysis No. 42. Also contains CO_2, 0.02; SO_3, trace; BaO, 0.05; SrO, trace.
9. Tektite, Peru. Linck, G., *Neues Jahrb. Mineral., Geol.*, **57**, 223 (1928).
10. Pitchstone, Madagascar. HSW, 144, Analysis No. 252. Also contains P_2O_5, 0.09.
11. Pitchstone, Iceland. HSW, 232, Analysis No. 108.
12. Rhyolite-dacite obsidian, Big Butte, Mont. HSW, 220, Analysis No. 28. Also contains P_2O_5, 0.12; MnO, trace; Cl, 0.05; BaO, 0.11; SrO, 0.03.
13. Pitchstone, Boggabri, New South Wales. HSW, 102, Analysis No. 26. Also contains CO_2, trace.
14. "Pierres de foudre," from fusion of grain ash. Velain, Ch., *Bull. franc. soc. mineral.*, **1**, 113 (1878). Also contains P_2O_5, 7.2.
15. Trachyte, Heard Island, Indian Ocean. HSW, 428, Analysis No. 47.
16. Fulgurite, Little Ararat, Armenia. HSW, 1032, Analysis No. 158. Also contains P_2O_5, 0.19; MnO, 0.18.
17. Obsidian, Mt. Vesuvius, Italy. HSW, 582, Analysis No. 1.
18. Pele's hair, Kilauea, Hawaiian Islands. HSW, 1109, Analysis No. 218. Also contains P_2O_5, 0.26; MnO, 0.41.

lightning, a fulgurite was popularly supposed to be the remains of the lightning bolt. Myers and Peck[9] described an excellent example found in a sand-pit at South Amboy, N. J. The fragments recovered represented a total length of nine feet. The greatest diameter was three inches, which gradually decreased to three-sixteenths of an inch. The surface was exceedingly rough, and the interior was white from included bubbles. The glassy wall consisted of 99 per cent SiO_2, with 0.7 per cent Al_2O_3, and 0.3 per cent Fe_2O_3, and it had a refractive index of $n_D = 1.462 \pm 0.003$.

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[9] Myers, W. M., and Peck, A. B., *Am. Mineral.*, **10**, 152 (1925).

Fulgurites usually are high in silica, representing fused sand or sandstone; but significant amounts of other minerals, especially feldspar, are sometimes present in the sand and enter the glass. Rarely the fulgurites have a very different composition, for example, those found on the summit of Little Ararat, Armenia (No. 16, Table III. 1), which contain less than 60 per cent SiO_2.

Suess[10] coined the term *tektite* to designate a group of natural glasses found in many parts of the world. The group included the shonites of Sweden, the moldavites of Central Europe, the billitonites of the East Indies, the australites of Australia, and Darwin glass of Tasmania. David, Summers, and Ampt[11] suggested that the area of distribution of the tektites is roughly on a great circle, but Janoschek[12] did not agree. The tektites usually have been considered of meteoric origin, and several hypotheses have been offered to explain them. Linck[13] considered that they are volcanic bombs shot from the moon during the Pleistocene periods; Chapman,[14] that they are aerial fulgurites resulting from the fusion by lightning of dust in the air, a view with which Fenner[15] appeared to concur.

Spencer[16] said, "The meteoric theory of the origin of tektites is certainly one that appeals to the imagination, but in reality there is not a single item of fact that can be adduced in its favor." He considered that they are formed by the impact of meteors on sand or sandstone, producing a pool of molten silica, more or less pure, which then is shaped by splashing for a great distance through the air. The silica glass fragments from the Libyan desert described by Clayton and Spencer[17] may have been formed in this manner. They are lumps of silica glass scattered over an area of 25 to 80 kilometers in a region of regular sand dunes in parallel ridges, 2 to 5 kilometers apart. The lumps range from tiny bubbles to pieces 10 pounds in weight; they are colorless, isotropic, and $n_D = 1.4624$. The silica glass found in masses up to 15 cm. in thickness in the bottom of Meteor Crater, Arizona,[18] probably was formed by the impact of a meteor on the saccharoidal sandstone.

It should not be inferred that tektites are always, or usually, pure silica, despite Spencer's statement: ". . . The elementary fact that the material of which they are composed is really an impure silica-glass has been entirely overlooked . . ." In the next paragraph he cites the analyses of "silica-glass" formed by meteoric impact, found in the " 'cinders

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[10] Suess, F. E., *Mitt. Geol. Ges. Wien*, **7,** 54 (1914).

[11] David, T. W. E., Summers, H. S., and Ampt, G. A., *Proc. Roy. Soc. Victoria*, **39,** 157 (1927).

[12] Janoschek, R., *Mineral. Abstracts*, **6,** 18 (1935).

[13] Linck, G., *Neues Jahrb. Mineral, Geol., Beilage Bd.*, **57,** 223 (1928).

[14] Chapman, F., *Nature*, **131,** 876 (1933).

[15] Fenner, C., *Nature*, **132,** 571 (1933).

[16] Spencer, L. J., *Nature*, **131,** 117 and 876 (1933).

[17] Clayton, P. A., and Spencer, L. J., *Mineral. Mag.*, **23,** 501 (1934).

[18] Rogers, A. F., *Am. J. Sci.*, **19,** 195 (1930).

of the legendary city of Wabar,' destroyed by fire from heaven," in the Rub al Khali, Arabia; "the black glass almost free from bubbles, contains SiO_2, 87.45 per cent." He also cites the "silica-glass" found near Henbury, Australia. Here the country-rock is a ferruginous sandstone, and the black glass contains 68.88 per cent SiO_2, $n_D = 1.545$. There is no doubt that many tektites are high in silica, but many contain only about 70 to 75 per cent SiO_2, and cannot be regarded even as "impure" silica glass. Analyses of typical tektites are given in Table III. 1.

Glass frequently is found as a constituent of eruptive rocks, sometimes in enormous quantities. The famous Obsidian Cliffs of Yellowstone Park are composed almost entirely of glass (No. 5, Table III. 1), and contain only a small amount of crystalline material. The obsidian from Cerro de los Navajo (No. 6), used by the Aztecs for making razors and sacrificial knives, is of similar composition. Most natural glasses resemble granite in composition, and represent material which under other conditions would have solidified to a crystalline rock, but because of rapid cooling has become a glass. Basaltic glass is less common: Nos. 17 and 18 are examples. No. 17 is from the 1906 eruption of Vesuvius, and No. 18 is volcanic glass fiber, "Pele's hair," formed by winds drawing out fibers of glass from lava blown into the air by bursting bubbles in the crater of Kilauea. Some glasses contain large amounts of water, as illustrated by Nos. 7, 8, and 13 of Table III. 1.

The properties of natural glasses have been discussed by Stark,[19] by Tilley,[20] and by George [21] with special reference to density and refractive index. Hawkes [22] discussed the natural glasses with special reference to the so-called transition of glass.

Commercial Glass

The essential requirements of a commercial glass composition are that it be fluid enough at an industrially accessible temperature to be melted on a commercial scale; viscous enough to be worked above its freezing point, so that devitrification cannot take place; so viscous at its freezing point that it will not devitrify; and that the resulting glass have physical properties and chemical durability suitable for the purpose for which it is intended.

Silica is the outstanding glass-forming oxide, for silica glass possesses in the highest degree the desirable qualities of freedom from devitrification, resistance to attack by water and by acids, and low coefficient of expansion. If it were not so difficult to melt quartz, to free it from

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[19] Stark, M., *Tschermak's Mineralog. Petrog. Mitt.*, **23**, 536 (1904).

[20] Tilley, C. E., *Mineralog. Mag.*, **19**, 275 (1922).

[21] George, W. O., *J. Geol.*, **32**, 353 (1924).

[22] Hawkes, L., *Geolog. Mag.*, **67**, 17 (1930).

bubbles and to work it, silica glass* would be the most suitable material for most of the uses to which glass is put. Sosman,[23] in his monumental treatise on the properties of silica, has discussed critically the experimental work on silica glass, as well as on the crystalline forms of silica. His conclusions are quoted frequently in this book.

The difficulty and cost of manufacture make silica glass impossible to use for general purposes, and other oxides must be added to flux the silica and reduce the viscosity. It might be thought that the natural glasses could be imitated. Natural glass of the composition of obsidian (Table III. 1) is highly resistant to devitrification and to weathering, and would be a desirable glass if it could be manufactured at a suitable cost. Obsidian may be considered as a mixture of alkali feldspar and silica. The soda feldspar, albite, has the composition $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, and if the alumina were replaced by lime, giving $Na_2O \cdot CaO \cdot 6SiO_2$, the composition would be near the most favorable glass field. But obsidian cannot be imitated by the glass manufacturer, and the alkali feldspar glasses are not suitable for commercial glass because of their enormous viscosity.** The soda feldspar, albite, has a true melting point at 1122°, and the potash feldspar, orthoclase, melts with decomposition at 1170°. But at 1200° albite glass has a viscosity of 10 million poises and orthoclase glass a viscosity of 300 million poises. An ordinary soda-lime glass has a viscosity of about 10 to 50 poises at the temperature at which it is melted, of about 300 poises at 1200°, and does not attain a viscosity of 10 million poises until it has cooled to about 800°.

The most effective flux for silica is soda, Na_2O, usually added in the form of sodium carbonate. Sodium silicate glass, of about the composition of the lowest-melting composition between sodium disilicate and quartz,[24] is made in large quantity in the soluble silicate industry. It is readily dissolved by water, and some other oxide must be added to give it better chemical durability if a permanent glass is to be obtained. The oxide commonly added is lime, CaO, because it is cheap and efficacious. If too little lime is added, the glass, although easy to melt,

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* Glass composed of silica alone is properly termed "silica glass," whether made from precipitated silica, silica gel, or any other of the amorphous forms of silica, or from quartz, tridymite, or cristobalite, the crystalline forms of silica. It is made usually from quartz, because quartz is cheap, and obtainable in quantity in a degree of purity equalled by few raw materials. The terms "quartz glass" or "fused quartz," while not in themselves objectionable, are better avoided. The not infrequent practice of speaking of silica glass as quartz, for example, of referring to apparatus as constructed of quartz when it is made from fused silica, cannot be too strongly deprecated. Inasmuch as apparatus sometimes is constructed with quartz parts, it is often necessary to infer from the context which material was actually used, and sometimes that is not possible.

[23] Sosman, R. B., "The Properties of Silica"; Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

** See p. 169.

[24] Cf. the discussion, p. 44.

has poor chemical durability. Much of the ancient Egyptian glass which has survived probably represents their best product, yet their best was of so poor a quality as to be rejected by discriminating users today, because of its high content of sodium oxide. An example of a commercial glass lacking in durability is No. 1 of Table III. 2. Greater durability is obtained by adding more lime; but too much results in a glass hard to melt and sure to devitrify. Increasing the quantity of silica also improves the chemical durability, but results in a glass hard to melt and with a tendency toward devitrification. The best composition for a pure soda-lime-silica glass is near the boundary (*PQ* in Fig. II. 8) between the fields of silica and devitrite, that is, one with a

TABLE III. 2—Compositions of Some Commercial Glasses

<table>
<tr><th>No.</th><th>SiO_2</th><th>Na_2O</th><th>K_2O</th><th>MgO</th><th>CaO</th><th>PbO</th><th>Al_2O_3</th><th>Fe_2O_3</th></tr>
<tr><td>1</td><td>68.0</td><td>22.0</td><td></td><td></td><td>7.2</td><td></td><td colspan="2">3.1</td></tr>
<tr><td>2</td><td>68.76</td><td>14.96</td><td>3.04</td><td>0.38</td><td>7.15</td><td></td><td>4.79</td><td>0.14</td></tr>
<tr><td>3</td><td>72.26</td><td>14.01</td><td></td><td></td><td>13.34</td><td></td><td colspan="2">1.42</td></tr>
<tr><td>4</td><td>69.65</td><td>15.22</td><td></td><td></td><td>13.31</td><td></td><td colspan="2">1.82</td></tr>
<tr><td>5</td><td>72.68</td><td>13.25</td><td></td><td>0.26</td><td>12.76</td><td></td><td colspan="2">1.06</td></tr>
<tr><td>6</td><td>71.82</td><td>14.27</td><td></td><td>3.31</td><td>8.90</td><td></td><td>1.40</td><td>0.07</td></tr>
<tr><td>7</td><td>70.51</td><td>16.74</td><td></td><td></td><td>10.67</td><td></td><td>1.42</td><td>0.16</td></tr>
<tr><td>8</td><td>70.64</td><td>17.02</td><td></td><td>0.09</td><td>10.58</td><td></td><td>0.77</td><td>0.11</td></tr>
<tr><td>9</td><td>72.14</td><td>12.60</td><td></td><td>2.62</td><td>11.24</td><td></td><td>1.06</td><td>0.15</td></tr>
<tr><td>10</td><td>64.30</td><td>5.87</td><td>2.56</td><td>5.61</td><td>14.73</td><td></td><td>4.89</td><td>1.18</td></tr>
<tr><td>11</td><td>63.18</td><td>9.88</td><td>0.36</td><td>1.12</td><td>14.40</td><td></td><td>8.39</td><td>1.93</td></tr>
<tr><td>12</td><td>71.28</td><td>12.13</td><td>1.01</td><td>3.19</td><td>3.87</td><td></td><td colspan="2">1.92</td></tr>
<tr><td>13</td><td>74.0</td><td>17.0</td><td></td><td>3.5</td><td>5.0</td><td></td><td colspan="2">0.5</td></tr>
<tr><td>14</td><td>63.0</td><td>7.6</td><td>6.0</td><td>0.2</td><td>0.3</td><td>21.0</td><td colspan="2">0.6</td></tr>
<tr><td>15</td><td>56.5</td><td>5.4</td><td>8.6</td><td></td><td></td><td>29.5</td><td></td><td></td></tr>
<tr><td>16</td><td>72.1</td><td>21.1</td><td></td><td>1.95</td><td>2.77</td><td></td><td>2.0</td><td></td></tr>
<tr><td>17</td><td>73.6</td><td>17.23</td><td></td><td>3.67</td><td>5.37</td><td></td><td></td><td></td></tr>
<tr><td>18</td><td>74.2</td><td>17.7</td><td></td><td>3.2</td><td>4.3</td><td></td><td></td><td></td></tr>
<tr><td>19</td><td>67.2</td><td></td><td>7.1</td><td>9.5</td><td>0.9</td><td>1.48</td><td></td><td></td></tr>
</table>

1. Christmas-tree ornament. Glass No. 69, Sharp, D. E., *Ind. Eng. Chem.*, **25**, 755 (1933).
2. Thuringian glass, Zschimmer, E., *Sprechsaal*, **57**, 301 (1924). Also contains Mn_2O_3, 0.40.
3. American window glass, hand cylinder process. Glass No. 7, Sharp, D. E., *Ibid.*
4. French window glass, hand cylinder process. Glass No. 10, Sharp, D. E., *Ibid.*
5. German window glass, hand cylinder process. Glass No. 11, Sharp, D. E., *Ibid.*
6. Flat-drawn window glass, American Fourcault process. Glass No. 15, Sharp, D. E., *Ibid.* Also contains SO_3, 0.31.
7. Belgian Fourcault. Glass No. 19, Sharp, D. E., *Ibid.* Also contains SO_3, 0.93.
8. Flat-drawn window glass, Libbey-Owens process, European. Glass No. 25, Sharp, D. E., *Ibid.* Also contains SO_3, 0.85; MnO, 0.05.
9. Flat-drawn window glass, Libbey-Owens process, American. Glass No. 28, Sharp, D. E., *Ibid.* Also contains SO_3, 0.47.
10. Bottle, light green. Glass No. 36, Zschimmer, E., *Ibid.*
11. Champagne bottle. Glass No. 40, Zschimmer, E., *Ibid.* Also contains Mn_2O_3, 0.12.
12. American vacuum bottle. Glass No. 63, Sharp, D. E., *Ibid.* Also contains B_2O_3, 4.70; ZnO, 1.21; As_2O_3, 0.13.
13. Representative machine-made container glass. Sharp, D. E., *Ibid.*, Table V.
14. American lead bottle glass. Glass No. 55, Sharp, D. E., *Ibid.* Also contains MnO, 0.2; As_2O_3, 0.05.
15. German lead bulb glass. Glass No. 52, Sharp, D. E., *Ibid.*
16. Lime bulb glass. Glass No. 61, Sharp, D. E., *Ibid.*
17. Lime bulb glass, Westlake machine, calc. from batch. Glass No. 62, Sharp, D. E., *Ibid.*
18. Lime crystal glass. Glass No. 70, Sharp, D. E., *Ibid.* Also contains B_2O_3, 0.4; As_2O_3, 0.2.
19. Light lead crystal. Glass No. 72, Sharp, D. E., *Ibid.* Also contains As_2O_3, 0.5.

SiO_2 content of from 73 to 74 per cent, and a CaO content of from 7 to 13 per cent. Glasses near the boundary (*RN*) between devitrite and $Na_2O \cdot 2CaO \cdot 3SiO_2$ are too readily attacked by water, unless they approach *R* in composition, when they become devitrified too easily.

The glass manufacturer is aided by the fact that he is never dealing with pure soda-lime glasses, but always with glasses containing small amounts of other constituents, which are either introduced deliberately, or incidentally by impurities in the batch ingredients, or by pot or tank corrosion. Some magnesia, MgO, is usually present; it can be substituted for lime with advantage, provided the proportion is not too large. A dolomitic limestone is used frequently in this country, much less frequently in Europe.

Alumina in small quantity is a frequent constituent of glass. It gives greater chemical durability, lower coefficient of expansion, and greater freedom from devitrification. The deliberate addition of alumina was the result of a research by Schott,[25] who showed that the superiority for table and blowpipe working of certain glasses made in the Thuringian Forest (*e. g.* No. 2, Table III. 2) was caused by the presence of almost 4 per cent of alumina in the Martinsroda sand used, and that addition of alumina to the usual glass batches greatly diminished the tendency toward devitrification of the resulting product. Too much alumina, however, increased the viscosity of the glass, making it difficult to melt and work.

The use of a small proportion of potash is also beneficial both in increasing the chemical durability and in diminishing the tendency toward devitrification, but the resulting increased viscosity may necessitate a higher melting temperature. Small amounts of barium oxide and of boric oxide frequently are added for the same reason. They are comparatively expensive ingredients; and a large proportion of any one of them produces some unfavorable result.

The composition of glass used for all of the great mass production industries is much the same. Sharp[26] gave as the most representative composition of both window and plate glass at the beginning of the present century: SiO_2, 71.5 per cent; Al_2O_3, 1.5; Na_2O, 14.0; CaO, 13.0. Some examples of commercial ware are Nos. 3, 4, and 5 of Table III. 2. The introduction of continuous machine processes made necessary the development of types of glass adapted to the characteristics of the various machines and types of ware; and further made necessary more precise control of the composition and properties of the glass. A hand operative can make allowances for differences in his glass, but the machine must have glass of constant and definite properties. In the continuous

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[25] Schott, O., "Verhandl. Ver. Beförd. Gewerbefleisses," 799 (1887).

[26] Sharp, D. E., *Ind. Eng. Chem.*, **25**, 755 (1933). This paper contains an excellent collection of glass compositions.

machine processes for making window and plate glass, conditions usually are more favorable for devitrification than in the older processes, and the compositions given above require modification. In Europe, the tendency has been to increase the soda and alumina contents. In America, the increase in soda has been smaller; the alumina content has been increased; and magnesia has been substituted for part of the lime. Recently some firms have added small amounts of barium oxide, or boric oxide, or of both. Each of these lowers the liquidus temperature and thus decreases the tendency toward devitrification. Examples of modern machine-made flint glass are Nos. 6 to 9 of Table III. 2.

Hollow ware, especially containers such as bottles and jugs, still are made to some extent by hand, in spite of the lower cost of ware made by machine in large quantity. Examples of old types of hand-blown glass are Nos. 10 and 11 of Table III. 2. No. 12 is a vacuum-bottle; No. 13 was given by Sharp as representative of modern machine-made container glass.

Electric light bulbs were made formerly from a glass containing lead oxide, of about the same composition as is used for cut glass and for "lead" tubing (Nos. 13 to 15, Table III. 2). Sharp gave the following as the range of composition of modern lead bulb glass in percentage by weight: SiO_2, 58 to 59; Na_2O, 7 to 8; K_2O, 4 to 5; PbO, 28 to 30; Al_2O_3, 0.2 to 0.4; and Fe_2O_3, 0.04 to 0.06. The development by Corning Glass Works[27] of a lead-free glass suitable for machine production of electric light bulbs was one of the important post-war developments in America (Nos. 16 and 17, Table III. 2). Sharp gave as the range of composition of modern lime bulb glass: SiO_2, 71.5 to 73.5; Na_2O, 14 to 17; K_2O, 0.0 to 1.5; MgO, 3.5 to 4.5; CaO, 5 to 6; Al_2O_3, 1 to 2; and Fe_2O_3, 0.06 to 0.1.

Tableware is largely of the same general composition as most soda-lime glasses, as is shown by No. 19, Table III. 2. In the more expensive grades some lead oxide is used (No. 20). The best "crystal," both plain and cut (No. 21), contains from 15 to 30 per cent PbO, or even more (No. 22), and the alkali is potash, K_2O, because of the greater brilliancy of the potash glasses.

Glass for laboratory use represents a special type, for it must be especially resistant to decomposition by water and by acids. Stas,[28] in 1868, found the available glassware too readily dissolved to be suitable for his researches on atomic weights, and developed a composition suitable for the purpose (No. 1, Table III. 3). It was characterized by the presence of both potash and soda, and by high silica content. It was a difficult glass to manufacture at that time, and did not become a com-

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[27] Sullivan, E. C., and Taylor, W. C., U. S. Patent 1,369,988 (1921).

[28] Stas, J. S., *Chem. News*, 17, 1 (1868).

TABLE III. 3—Compositions of Some Laboratory and Resistant Glasses

No.	SiO_2	B_2O_3	Na_2O	K_2O	MgO	CaO	ZnO	Al_2O_3	Fe_2O_3
1	77.0		5.0	7.7		10.3			
2	79.4		6.4	6.7		7.6			
3	75.9		7.1	7.9	0.17	8.7		0.14	0.08
4	66.4	4.0	15.6		5.2		6.2	2.4	
5	64.7	10.9	7.5	0.37	0.21	0.63	10.9	4.2	0.25
6	73.0	3.6	10.8	0.30	4.3	0.66	5.6	1.0	0.35
7	67.3	6.2	10.9	0.30	3.4	0.79	7.8	2.5	0.23
8	66.80	4.13	7.40	1.75	2.60	1.73	9.75	2.54	0.17
9	75.90		7.29	7.84	0.15	8.73		0.24	0.10
10	76.20		7.07	7.62		8.97		0.30	0.14
11	74.32		17.56	1.38	0.11	3.67		2.35	0.14
12	77.9	14.1	4.1	2.3		0.8		0.8	
13	81.5	11.0	3.7	0.9		0.3		2.8	
14	81.4	10.6	4.4	1.1		0.7		2.0	
15	75.3	15.8	3.4	1.0		1.3		2.5	
16	75.4	17.5	3.6	0.4		0.1		1.6	
17	75.3	7.6	5.7	0.8		1.1		6.2	
18	57.4	23.6	1.9	0.5	8.7	4.7		3.2	
19	75.6	14.3	3.3	0.4		0.1		5.6	
20	80.5	12.9	3.8	0.4				2.2	

1. Stas' apparatus glass. Glass No. 73, Sharp, D. E., *Ind. Eng. Chem.*, **25**, 755 (1933).
2. Kavalier glass, 1879. Glass No. 74, Sharp, D. E., *Ibid.*
3. Kavalier beaker. Walker, P. H., and Smither, F. W., Tech. Paper. No. 107, Nat. Bur. Standards, 1918. Also contains MnO, 0.02; P_2O_5, 0.08; SO_3, 0.20; As_2O_5, trace.
4. Jena Gerate, prior to 1910. Glass No. 75, Sharp, D. E., *Ibid.*
5. Jena Gerate beaker, Walker, P. H., and Smither, F. W., Ibid. Also contains MnO, 0.01; As_2O_5, 0.14.
6. Macbeth-Evans beaker, 1918. Walker, P. H., and Smither, F. W., *Ibid.* Also contains MnO, 0.02; SO_3, 0.02; As_2O_5, 0.02; Sb_2O_3, 0.60.
7. Nonsol beaker, 1918. Walker, P. H., and Smither, F. W., *Ibid.* Also contains MnO, 0.01; Sb_2O_3, 0.62.
8. Kohln-Ehrenfeld. Cauwood, J. D., and Turner, W. E. S., *J. Soc. Glass Tech.*, **2**, 219 (1918). Also contains As_2O_3, 2.05; Sb_2O_3, 1.29.
9. Resistance, "R". Cauwood, J. D., and Turner, W. E. S., *Ibid.* Also contains As_2O_3, trace; MnO, 0.13.
10. Zsolna. Cauwood, J. D., and Turner, W. E. S., *Ibid.* Also contains Sb_2O_3, 0.30.
11. Japanese. Cauwood, J. D., and Turner, W. E. S., *Ibid.* Also contains MnO, 0.10.
12. Silex. Thiene, H., *Z. angew. Chem.*, **39**, 193 (1926).
13. Vulkanite. Thiene, H., *Ibid.*
14. Resista, 1923. Thiene, H., *Ibid.*
15. Resista, 1925. Thiene, H., *Ibid.*
16. Tempax. Thiene, H., *Ibid.* Also contains Sb_2O_3, 1.6.
17. Jena Gerate, 1920. Thiene, H., *Ibid.* Also contains BaO, 3.5.
18. Jena Supremax 1565^{III}. Thiene, H., *Ibid.*
19. Jena Durax 3817^{III}. Thiene, H., *Ibid.* Also contains Sb_2O_3, 0.4.
20. Pyrex chemical resistant glass.

mercial type. The Kavalier glass later developed for high-temperature work (Nos. 2 and 3, Table III. 3) was of similar composition. The first Jena "Geräte" glass, made before 1910 (No. 4, Table III. 3), differed from the ordinary soda-lime glass in the substitution of magnesia and zinc oxide for lime, and in having a small content of B_2O_3. Later (No. 15, Table III. 3) the soda content was reduced and the magnesia largely removed, with increase in the zinc oxide, alumina and boric oxide. The compositions of some other types of laboratory glassware are shown in Table III. 3. They have been displaced largely by "Pyrex" resistant laboratory glass * (No. 20, Table III. 3), which is fundamentally different from the usual soda-lime-silica composition. It is better considered to be a glass in which the melting point of the silica has been lowered by the addition of B_2O_3, and, in smaller amount, of alumina, with only the smallest possible amount of alkali. It is intrinsically superior to the best glasses of the soda-lime group in its chemical durability and in its resistance to breakage from heat shock or mechanical strain, but it is more difficult to manufacture and to work.

The optical glasses have the greatest diversity in composition because of the lens designer's need for the widest range in optical properties. They are characterized by almost perfect freedom from physical defects, and their quality represents the highest achievements of the glassmaker. They are discussed in greater detail in Chapter XVI; Tables XVI. 22 and 23 give approximate compositions of representative types of optical glasses. Table III. 4 gives compositions of some optical and other glasses manufactured by Schott u. Gen., on which numerous measurements of physical properties have been made. Some of these measurements are shown in Table I. 2; others are in their appropriate places in the various chapters.

The compositions of the glasses in Table III. 4 were collected from several sources, and the composition given is usually that of the type of glass, not of the sample on which the measurement was made. Many of the analyses were taken from an article by Zschimmer,[29] who was for many years associated with Schott u. Gen. at Jena; and many of the measurements on these glasses, as well as some of the compositions, were taken from the well-known treatise by Hovestadt [30] on the scientific work carried on at Jena by Schott, Winkelmann and their collaborators. Most of the compositions from these two sources have been republished by Wright [31] and by Morey,[32] and they were the source of most of the

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* There is confusion in the literature arising from authors' assuming that "Pyrex" is sufficient to describe adequately the composition of a glass. "Pyrex" is not the name of a material but is a trade mark of the Corning Glass Works covering various thermally, electrically, or chemically resistant glasses of different compositions. The type commonly used for chemical ware is the "Pyrex chemical resistant glass," Code No. 774. This is glass No. 20 of Table III. 3, sometimes referred to as No. 702 EJ. Pyrex baking ware is made usually from the same glass as Pyrex chemical ware, but it has not been confined exclusively to this composition. Arsenic oxide has been eliminated ** from all baking ware and from chemical glassware; with this exception, the composition of Pyrex chemical resistant glass has remained unchanged.

** Taylor, W. C., *Ind. Eng. Chem., News Ed.*, **14**, 23 (1936).

[29] Zschimmer, E., in Doelter, C., "Handbuch der Mineralchemie," **1**, 869, T. Steinkopff, Dresden u. Leipzig, 1912.

[30] Hovestadt. H., "Jenaer Glas und seine Verwendung in Wissenschaft und Technik," Gustav Fischer, Jena, 1900. Translation by Everett, J. D. and A., Macmillan, New York, 1902.

[31] Wright, F. E., "The Manufacture of Optical Glass and of Optical Systems," *U. S. Ordnance Department, Document No. 2037*, Govt. Print. Off., Washington, 1921.

[32] Morey, G. W., "Properties of Glass," *International Critical Tables;* **2**, 87, McGraw-Hill, New York, 1927.

TABLE III. 4A—Compositions of Some Experimental, Optical, and Commercial Glasses

No.	Type	Name			Lit. ref.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	PbO	Al_2O_3	Fe_2O_3
1	496/644	Borosilicate crown	BK3	O802	1	71.0	14.0	10.0						5.	
2	494/646	Borosilicate crown		O2259	2	69.59	14	8	3					8	
3	506/602	Crown		O714	3	74.6		9	11	5					
4	511/640	Borosilicate crown	BK1	O144	3	70.4	7.4	5.3	14.5	2					
4a	*510/640*	*Same, analysis*			4	*72.15*	*5.88*	*5.16*	*13.85*	*2.04*	*0*	*0*	*Trace*	*0.04*	*0.01*
5	511/605	Borosilicate crown		O374	3	68.1	3.5	5.0	16.0			7.0			
6	513/637	Borosilicate crown		O627	3	68.2	10.0	10.0	9.5			2.0			
7	513/573	Zinc silicate crown	ZK6	O709	1	70.6		17.0				12.0			
8	516/640	Borosilicate crown	BK7	O3832	4	69.58	9.91	8.44	8.37	0.07	2.54	0	0	0.04	0.01
9	516/536	Borosilicate crown		O608	3	53.5	20.0		6.5						
10	516/609	Silicate crown		O40	3	69.0	2.5	4.0	16.0	8.					
11	517/602	Silicate crown		O60	3	64.6	2.7	5.0	15 0		10.2	2.0			
12	517/558	Light barium crown		O1092	5	65.4	2.5	5.0	15.0		9.6	2.0			
13	520/520	High dispersion crown	KF2	O381	3	66.8		16.0				3.8	11.6	1.5	
13a		*Same, analysis*			6	*67.40*		*15.15*	*0.14*	*0.39*		*3.85*	*10.71*	*1.72*	*0.02*
14	517/602	Zinc crown	2K2	O546	3	65.6	4.5	14.5	3.5			11.5			
15	522/596	Silicate crown	K5	O1282	7	62.5	2.0	5.0	15.0		11.0	3.0	1.0		
16	537/512	Borosilicate flint	KF1	O152	8	35.4	34.3	7.4					18.7	3.7	
17	540/598	Light barium crown	BaK2	O227	3	59.5	3.0	3.0	10.0		19.2	5.0			
17a	*541/596*	*Same, analysis*			4	*59.13*	*3.04*	*3.16*	*9.70*	*0.13*	*19.25*	*5.0*	*0*	*0.11*	*0.02*
18	541/469	Light flint	LLF2	O726		62.6		4.5	8.5				24.1		
19	545/503	Light borosilicate flint		O658	1	32.75	31.	1	3				25.	7.	
20	549/461	Extra-light flint	LLF1	O378	3	59.3		5	8				27.5		
21	553/530	Light barium flint	BaLF5	O846	3	56.2		1.5	11		15	9	7.		
22	563/497	Light barium flint	BaLF1	O543	3	51.6		1.5	9.5		14	12	11.		
23	568/467	Light borosilicate flint		O161	3	29.0	29.0	1.5					30.0	10.0	
24	568/530	Light barium flint	BaLF3	O602	3	51.2		5.5	5.0		20	14	4		
25	571/430	Light flint	LF1	O154	3	54.3	1.5	3.0	8.0				33.0		
25a	*571/430*	*Same, analysis*				*54.75*	*0.45*	*4.31*	*7.99*	*0.05*	*1.64*	*0.96*	*29.30*	*0.04*	*0.02*
26	572/504	Light barium flint		O527	3	51.7		1.5	9.5		20.0	7.0	10.0		
27	573/574	Light barium crown	BaK1	O211	3	48.1	4.5	1.0	7.5		28.3	10.1			
27a		*Same, analysis*			6	*47.73*	*3.90*	*1.14*	*7.16*	*0.15*	*29.88*	*8.61*		*0.65*	*0.01*
28	576/408	Light flint	LF2	O184	3	53.7		1.0	8.3				36.6		
29	579/541	Light barium crown		O722	3	48.8	3.0	0.8	6.5		21.0	15.5	4.1		
29a	*580/538*	*Same, analysis*			4	*46.02*	*4.50*	*0.64*	*6.80*		*22.39*	*15.53*	*4.70*	*0.09*	
30	581/422	Ordinary light flint	LF3	O276	7	52.45		4.5	8.0				34.8		
31	583/469	Light barium flint	BaF3	O578	3	49.1		1.0	8.5		13.0	8.5	19.3		
31a	*583/463*	*Same, analysis*			4	*49.80*		*1.24*	*8.20*		*13.36*	*8.03*	*18.74*	*0.05*	*0.01*
32	591/605	Dense barium crown	SK5	O2122	3	37.5	15.0				41.0			5.0	
33	604/438	Barium flint	BaF4	O1266	3	45.2			7.8		16.0	8.3	22.2		
34	610/574	Densest barium crown	SK1	O1209	3	34.5	10.1				42.0	7.8		5.0	
34a	*610/568*	*Same, analysis*			4	*40.17*	*5.96*	*0.13*	*0.03*	*0.03*	*42.35*	*8.17*	*None*	*2.79*	*0.02*
35	612/592	Densest barium crown	SK3	O2071	3	31.0	12.0				48.0			8.0	
35a	*609/588*	*Same, analysis*			4	*34.56*	*10.96*	*0.21*	*0.09*		*46.91*	*1.14*	*None*	*5.02*	
36	613/369	Ordinary silicate flint	F3	O118	3	46.6		1.5	7.8				43.8		

TABLE III. 4A—Compositions of Some Experimental, Optical, and Commercial Glasses—*(Continued)*

No.	Type	Name			Lit. ref.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	PbO	Al_2O_3	Fe_2O_3
36a		*Same, analysis*			6	*45.64*		*1.77*	*8.66*	*0.05*			*43.45*		*0.03*
37	621/361	Ordinary silicate flint	F2	O103	3	44.6		0.5	8.0				46.6		
38	627/391	Baryta flint	BaSF1	O748	3	42.8		0.7	7.5		10.8	5.1	32.6		
39	632/357	Ordinary silicate flint	F6	O919	6	44.		1.	7				48		
40	645/341	Heavy silicate flint	SF2	O102	3	41.			7				51.7		
40a	*649/338*	*Same, analysis*			6	*40.99*		*0.61*	*6.93*	*0.13*			*51.13*	*0.04*	*0.02*
41	680/317	Heavy silicate flint	SF5	O192	3	38.0			5.0				56.8		
42	717/295	Heavy silicate flint	SF1	O41	3	33.7			4.0				62.0		
43	755/275	Heavy silicate flint	SF4	O165	3	28.4			2.5				69.0		
44	778/265	Very heavy silicate flint	SF6	O198	3	27.3			1.5				71.0		
45	890/226	Very heavy silicate flint		S163	3	22.0							78.0		
46	905/217	Heaviest silicate flint		S208	3	20.0							80.0		
47	963/197	Heaviest silicate flint		S57	3	18.0							82.0		
48	507/614	Light borate crown		S205	3		69.1	8.0			4.7			18.0	
49	510/600	Borate crown		S204	3		63.8	8.0	3.5		3.5		3	18.0	
50	519/609	Borate crown		VS458	3		64.0							30.0	
51	523/614	Borate crown		S185	3		71.8							22.4	
52	573/469	Borate flint		VS428	3		56.0						32	12.0	
53	658/489	Zinc borate		S665	3		41.0					59.			
54	666/392	Borate flint		S120	3		42.8						52.0	5.0	
55		Exptl. glass No. 7		165^{III}	1	73.8		10.5		7.		5.0		3.5	
56	500/647	Borosilicate thermometer		59^{III}	1	72	12	11						5.0	
56a		*Same, analysis*			10	*72.86*	*10.43*	*9.82*	*0.10*	*0.35*				*6.24*	*Trace*
57		Experimental glass No. 34			1	70.2	12.0	10.3						4.5	
58		Experimental glass No. 90			12	69.5	2.0	7.0	16.0				2.5	2.5	
59		Experimental glass No. 8		1419	11	67.9		16.8				5.8	8.1	1.0	
60		Experimental glass No. 84			11	67.7	8.0	10.0				9.0			
61		Normal thermometer		16^{III}	1	67.3	2.0	14.0		7.0		7.0		2.5	
61a		*Same, analysis*			10	*66.58*	*0.91*	*14.80*	*Trace*	*7.18*		*6.24*		*3.84*	*Trace*
62		Jena combustion, analysis			12	66.90	7.22	1.25	2.40	7.94				6.38	0.22
63		Experimental glass No. 3		172^{III}	11	64.4	12.0	8.0						4.5	
64		Experimental glass No. 10		290	1	58.7			33.0	8.0					
65		Experimental glass No. 4		164^{III}	11	55.0		14.0	14.0					17.0	
66		Experimental glass No. 32			1	54.8			28.0			17.0			
67		Experimental glass No. 12		121^{III}	11	51.3	14.0				25.0	5.0		4.5	
68		Experimental glass No. 24			1	44.2		0.5	8.0				47.		P_2O_5
69		Experimental glass No. 23			1	34.5	10.2				42.0	7.8		5.0	
70	516/703	Light phosphate crown		O225	3		3.0		12.0					10.0	70.5
71	522/697	Light phosphate crown		S219	1		3.0		12.0					10.0	69.5
72	558/670	Phosphate crown		S206	1		3.0				28.0			8.0	59.5
73	563/646	Phosphate crown		S179	5		3.0				37.0			1.5	57.0
74	562/665	Phosphate crown		S40	9		3.0				28.0			5.0	59.5
75	567/650	Phosphate crown		S95	1		3.0				38.0			1.5	56.0

4a. Also contains MgO, 0.07; As_2O_5, 0.08; Cl, 0.06; SO_3, 0.12; H_2O, 0.08; MnO, none.

8. Also contains MgO, 0.07; As_2O_5, 0.09; Cl, 0.06; SO_3, 0.08; H_2O, 0.06; MnO, none.

9. Also contains Sb_2O_3, 20.0.

13a. Posnjak, E., analyst. Also contains Mn_2O_3, 0.04; H_2O, 0.15.

16. Also contains MgO, 0.5.

17a. Also contains As_2O_5, 0.34.

25a. Also contains As_2O_5, 0.14; As_2O_3, 0.06; Cl, 0.06; H_2O, 0.20; MgO and MnO, none.

27a. Allen, E. T., analyst. Also contains MgO, 0.02; As_2O_5, 0.38; H_2O, 0.14; SO_3, 0.04; Cl, 0.03.

29a. Also contains As_2O_5, 0.55; As_2O_3, 0.06; MnO, none.

31a. Posnjak, E., analyst. Also contains As_2O_5, 0.51; As_2O_3, 0.01; H_2O, 0.08; MnO, none.

34a. Also contains As_2O_5, 0.49; As_2O_3, 0.03; MnO, none. The difference in composition of 34 and 34a, both of the same type, probably represents intentional change.

35a. Also contains As_2O_5, 0.55; As_2O_3, 0.22.

36a. Allen, E. T., analyst. Also contains As_2O_3, 0.22.

40a. Posnjak, E., analyst. Also contains As_2O_3, 0.22.

50. Also contains Li_2O, 6.0.

51. Also contains Li_2O, 5.8.

56a. Also contains MgO, 0.20.

57. Also contains MgO, 3.0.

60. Also contains MgO, 5.0.

61a. Also contains MgO, 0.17; Mn_2O_3, 0.28.

62. Also contains MgO, 0.61.

63. Also contains MgO, 11.0.

70. Also contains MgO, 4.0; As_2O_3, 0.5.

71. Also contains MgO, 4.0; As_2O_3, 1.5.

72. Also contains As_2O_3, 1.5.

73. Also contains As_2O_3, 1.5.

74. Also contains As_2O_3, 1.5; D_2O_3, 3.0.

75. Also contains As_2O_3, 1.5.

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1. Winkelmann, A., and Schott, O., *Ann. Physik Chem.*, **51**, 697 (1894).
2. Sheen, A. R., and Turner, W. E. S., *J. Soc. Glass Tech.*, **8**, 187 (1924).
3. Zschimmer, E., in C. Doelter, "Handbuch der Mineralchemie," **1**, 869, Dresden and Leipzig, 1912.
4. Allen, E. T., and Zies, E. G., *J. Am. Ceram. Soc.*, **1**, 739 (1918).
5. Rubens, H., *Ann. Physik Chem.*, **45**, 238 (1892).
6. Wright, F. E., "The Manufacture of Optical Glass." Ordnance Dept. Document No. 2037 (1921).
7. Königsberger, J., *Ann. Physik Chem.*, **66**, 698 (1896).
8. Filon, L. N. G., *Proc. Camb. Phil. Soc.*, **12**, 313 (1904).
9. Pulfrich, C., *Ann. Physik Chem.*, **45**, 609 (1892).
10. National Physical Laboratory, *J. Soc. Chem. Ind.*, **34**, 210 (1915).
11. Hovestadt, H., "Jenaer Glass und seine Verwendung in Wissenschaft und Technik"; translation by J. D. and A. Everett; Macmillan, New York, 1902.
12. Branson, F. W., *J. Soc. Chem. Ind.*, **34**, 471 (1915).

TABLE III. 4B—Index to Properties of Glasses of Table III. 4A

Glass No.	See Table
1	I. 2; V. 8; IX. 1; XI. 19; XII. 9; XV. 1
2	XIX. 1
3	I. 2; XII. 9
4	I. 2; V. 8; XII. 9; XVI. 24; XIX. 1
5	XI. 19; XV. 1
6	I. 2; XI. 19; XVI. 28
7	I. 2; XII. 9; XV. 1
8	V. 8; IX. 1; XI. 19
9	I. 2
10	I. 2; XII. 9; XV. 1
11	I. 2; XI. 9; XII. 9; XVI. 28; XVII. 5
12	XVI. 24; XIX. 2
13	XI. 19; XVI. 26; XVIII. 2; XIX. 2
15	XIX. 1
17	XVI. 24
18	XVII. 5
19	XII. 9; XV. 1; XVI. 28; XIX. 1; XIX. 3
20	V. 8; XI. 19; XIX. 3
21	XVII. 5; XIX. 1
22	V. 8; XVI. 24
24	XVI. 26
26	XI. 19; XVI. 28; XIX. 3
27	I. 2; V. 8; XII. 9; XVI. 28; XVII. 5; XIX. 2
28	V. 8; XVI. 24; XIX. 2; XIX. 3
29	V. 8; XI. 19; XVI. 24
30	XIX. 1
31	XI. 19; XVI. 24; XIX. 1
32	V. 8; XI. 19; XVI. 24
33	XVI. 24; XVIII. 2
34	I. 2; V. 8; XVI. 24; XVI. 28; XVIII. 2
35	V. 8; XI. 19; XIX. 1
36	V. 8; XI. 1; XI. 19; XVI. 28; XVIII. 2; XIX. 3
37	XVI. 24
38	V. 8; XI. 19; XVI. 24
40	I. 2; V. 8; XI. 1; XI. 19; XII. 9; XV. 1; XIX. 2; XIX. 3
41	XIX. 1
42	V. 8; XI. 19; XIX. 3
43	I. 2; IX. 1; XI. 19; XII. 9; XV. 1; XVI. 24; XVI. 26; XIX. 2; XIX. 3
44	V. 8; XI. 19; XIX. 3
45	XVI. 24; XVI. 28; XIX. 2
46	I. 2; XV. 1; XIX. 3
47	X. 19; XVI. 28
48	I. 2; XII. 9; XV. 1; XVI. 28
49	XVI. 24; XIX. 2
50	I. 2; XI. 19
52	I. 2; XI. 19
53	I. 2; XI. 19
53	I. 2; XI. 19
55	I. 2; XII. 9
56	I. 2
57	I. 2; XII. 9
58	I. 2; XII. 9
59	I. 2; XII. 9
60	XII. 9; XVI. 24; XVII. 5
61	I. 2; XII. 9; XV. 1; XVII. 5
64	I. 2; XII. 9; XV. 1
66	I. 2; XII. 9
67	I. 2
68	I. 2; XII. 9
69	XII. 9; XV. 1
70	I. 2; IX. 1; XI. 19; XVI. 28
71	I. 2
72	I. 2; XII. 9; XV. 1
73	XVI. 24
74	XI. 19; XVI. 28; XIX. 2
75	I. 2

data given by Montgomery.[33] The compositions given in Table III. 4 usually were calculated from the ingredients of the batch that was melted, and differ from the true compositions by an unknown amount. Included in the same table, and indicated by italics, are some compositions determined by analysis. In some cases, usually of well-standardized types, the agreement between batch and analytical compositions is striking; in others the differences are so great as to indicate an alteration in the composition of that type of glass. Also, almost all of these glass batches included from 0.1 to 0.3 per cent As_2O_3,* and some of them contained

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[33] Montgomery, R. J., *J. Am. Ceram. Soc.*, **3**, 900 (1920); **4**, 536 (1921).

* The ingredient introduced into the batch is always As_2O_3, which is partially oxidized to As_2O_5. In all the tables As_2O_3 is given except when the As_2O_5 is determined as such by analysis, as in some of the glasses of Table III. 4.

a small amount, usually 0.1 per cent, of Mn_2O_3. These are not included, except when found by analysis.

In the introductory part of this section, the glass-forming oxides other than silica, namely, boric oxide and phosphoric oxide, were mentioned, and in the discussion of the silicate glasses, boric oxide was mentioned as a frequent constituent. Silicate-free borate and phosphate glasses have been made occasionally on a commercial scale, but they have not found a permanent place in the industry, except for some highly specialized uses. Table III. 4 contains a few silicate-free glasses produced for optical purposes.

Volatile Components in Glass

The work of many investigators has established that glass when heated gives off volatile substances, chiefly water and carbon dioxide, and that the gases given off may be grouped into two classes, one representing material adsorbed on the surface, and the other, material dissolved in the mass of the glass. The adsorption of gases on the surface of glass takes place after it has cooled; the dissolved gases are retained in the glass during cooling, and at the melting temperature were either in equilibrium with the furnace atmosphere, or so near equilibrium that their vapor pressure from the melt was not greatly in excess of their pressure in the furnace atmosphere.

The line of demarcation between the two classes is not sharp; at lower temperatures, up to 100° C., it is not feasible to remove all of the adsorbed material even by long-continued maintenance of high vacuum; at 200° to 300° C., depending on the type of glass, the greater part of the surface material is removed in a vacuum; with increasing temperature there is a continued evolution, which rapidly increases as the temperature is raised to that at which the glass becomes fluid. After the temperature interval in which the adsorbed gas comes off in greatest quantity, there may be evolution both of volatile substances truly adsorbed on the surface, and of volatile substances dissolved in the surface layer of the glass. The differentiation between the two classes then becomes one of arbitrary definition, unsupported by adequate experimental evidence.

The theoretical differentiation between the two classes likewise is not sharp. Adsorbed material often is considered to be fixed by secondary valence forces, and dissolved material by primary valence forces. Broadly speaking, this probably is correct; but in consideration of border-line cases, it is difficult to apply this criterion. Probably the loosest type of adsorption, that of an inert gas on a crystalline surface, is caused by stray electronic fields, and from such an adsorption to that of water combined with alkali in the form of sodium hydroxide, there is a continuous gradation. Concerning the water and carbon dioxide in solution in the glass, we have no definite information. They are probably "chemically combined" in the glass, just as are the sodium oxide and silicon dioxide; in other words, all the components of the glass are in a mutual solution in which it is not possible to identify any one-to-one coördination between the various groupings. Plausible though it may be to assume that the CO_2 in a barium glass is present as $BaCO_3$, there is no evidence which can be used for testing that assumption. Our knowledge of the constitution of solutions is too meagre to permit the identification of molecular groupings.

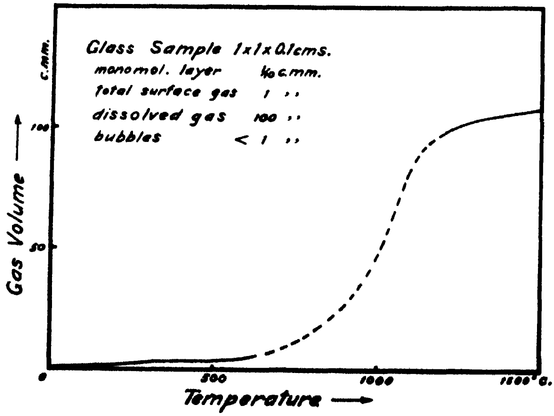

FIGURE III. 1.—Generalized Curve Showing the Volume of Gas Evolved from Glass, as affected by Temperature. After Dalton.

Figure III. 1, after Dalton,[34] shows in a general way the gas volumes evolved at various temperatures for a sample of glass 1 × 0.1 cm. The low foot at the beginning of the curve is due to the gas at or near the surface of the glass that came off below the softening point. At high temperatures where flow in glass became possible, the dissolved or chemically combined gases came off. The intermediate section of the curve is dotted to indicate that there were no actual observations in that neighborhood. The dissolved gases were of the order of 100 times the volume of the surface gas, if the sample was heated to glass furnace temperatures.

Adsorbed Volatile Substances

The presence on glass surfaces of films of volatile materials, chiefly water and carbon dioxide, has been known since the time of Bunsen,[35] who was the first to appreciate the importance of the adsorbed water film on the absorption of CO_2, and of heating glass apparatus used for

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[34] Dalton, R. H., *J. Am. Ceram. Soc.*, **16**, 425 (1933).

[35] Bunsen, R., *Ann. Physik Chem.*, **20**, 545 (1883); **22**, 145 (1884); **24**, 321 (1885).

quantitative work with gases to free it from adsorbed water. The subject did not become of general interest until the development of modern vacuum technique, and the extensive use of evacuated tubes in research and in industry.

Langmuir[36] considered that gaseous molecules impinging on a surface are condensed, "and are held or adsorbed on the surface by forces similar to those holding the atoms or group molecules of solid bodies. If these forces are weak, the 'life' of the adsorbed molecules on the surface is short, so that the number of molecules adsorbed at any time is relatively small. On the other hand, when the forces are strong, the rate of evaporation of the molecules may be so slow that the surface becomes covered by a monomolecular layer of adsorbed molecules."

Langmuir estimated the fraction of the saturated surface, β, at 90° K covered by adsorbed molecules, and found the amounts always less than needed to form a monomolecular layer. Values of β found for the various gases were: CO, 0.13 to 0.32; A, 0.20; O_2, 0.14; CH_4, 0.04 to 0.36; N_2, 0.26. The fact that β was so variable and so much less than unity suggested that the adsorption of most of the gases does not occur over the whole surface, but only where the arrangement of the surface atoms is such as to give particularly strong stray fields of force. Comparison of the relative "life" of a molecule, that is, the time in seconds required for the evaporation of one gram molecule per sq. cm., condensed on a glass surface, with that on the surface of the liquefied gas, at 90° K, showed the following ratios: N_2, 330,000; CH_4, 10,000; CO, 190,000; A, 73,000; O_2, 78,000; these indicate that the forces holding the molecules on a glass surface are much more intense than the forces holding them on a liquid surface.

The thickness of the adsorbed layer is in dispute. Bangham and Burt[37] found difficulty in reaching equilibrium in the adsorption and removal of CO_2, and found that the amount adsorbed greatly exceeded that required for a monomolecular film. McHaffie and Lenher[38] and Lenher[39] measured the change of pressure with temperature in bulbs containing sufficient water to condense on cooling. When vapor alone was present, the pressure-temperature curve was that given by the law of Gay-Lussac, $PV \propto T$; but after condensation took place, the subsequent pressure-temperature curve was the vapor pressure curve of water. If no adsorption took place, the two curves would intersect at a sharp angle; but adsorption caused it to be rounded, and from the amount of rounding, the adsorption was calculated. They found the adsorbed layers to range from 0 to 5.3×10^{-6} cm. in thickness, and to contain

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[36] Langmuir, I., *J. Am. Chem. Soc.*, **40**, 1361 (1918).

[37] Bangham, D. H., and Burt, F. P., *Proc. Roy. Soc. (London)*, *A*, **105**, 481 (1924).

[38] McHaffie, I. R., and Lenher, S., *J. Chem. Soc.*, **127**, 1559 (1925).

[39] Lenher, S., *J. Chem. Soc.*, **1926**, 1785; **1927**, 272.

from 0 to 2188 layers of molecules. The thickest layers corresponded to the saturation pressure of water.

The type of adsorption studied by McHaffie and Lenher may be different from that studied by Langmuir. Manley[40] found that a "nude" glass surface when brought into contact with glass acquired a "primary" gas skin, which was retained at high vacuum under ordinary conditions. This primary skin adsorbed a further quantity of gas to form a "secondary" skin, which was removable by continuous pumping. The manifold layers found by McHaffie and Lenher did not begin to be piled up until near the saturation pressure.

Frazer, Patrick, and Smith[41] claimed that glass surfaces which had been cleaned are no longer plane. They carried out adsorption measurements by the method used by McHaffie and Lenher on freshly-blown surfaces, which had been protected from moisture by having the glass-blower use a drying tube containing P_2O_5. Under these conditions, the thickness of an adsorbed film of toluene was never greater than one molecule, even at the saturation pressure. When water vapor was used with a freshly made surface, no film other than a monomolecular one was formed; but although the vapor pressure curves intersected at a sharp angle, the temperature of the intersection was lower than that which would have corresponded to the amount of water vapor present. This was considered to have been due to the reaction of the monomolecular layer with the glass, forming an alkaline solution with a vapor pressure lower than that of water. This reaction caused the surfaces no longer to be plane. The usual types of cleaning have the same effect. This renders vague and misleading the interpretation of all adsorption measurements made on such surfaces; and in particular, previous calculations of the thickness of such layers are in error because of lack of knowledge of the actual surface area.

Frazer[42] applied an optical method to the study of adsorbed films of water and methyl alcohol on glass. Up to five or six mm. pressure, there was no detectable adsorption of water vapor, apart from the probable presence of a monomolecular layer. Above that pressure, there was a cluster formation which resulted in the gradual covering of the surface, until at 12.5 mm. pressure there was another monomolecular layer present. At this pressure the film was about 30 mμ thick. Above 13 mm. pressure, there was strong condensation.

Sherwood[43] used a dynamic method for the estimation of the gases obtained from glass surfaces in vacuum, and found that there was a slow but persistent "leakage" of occluded gases exposed to a vacuum even at

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[40] Manley, J. J., *Proc. Phys. Soc. (London)*, **36**, 288 (1924).

[41] Frazer, J. C. W., Patrick, W. A., and Smith, H. E., *J. Phys. Chem.*, **31**, 897 (1927).

[42] Frazer, J. H., *Phys. Rev.*, **33**, 97 (1929).

[43] Sherwood, R. G., *Phys. Rev.*, **12**, 448 (1918); *J. Am. Chem. Soc.*, **40**, 1645 (1918).

room temperature, and that this leakage was more rapid for the inert gases than for vapors. A strong adsorbing action was found for glass toward water vapor or carbon dioxide, and a weak adsorbing action toward air. Dry air leaked off from a glass surface more rapidly than did moist air. A heat treatment as low as 200° C. was practically as effective as one at a higher temperature for the removal of adsorbed gaseous products. The inert gaseous layer was found to be of a thickness comparable to that of one molecule. Above 200° C. there was a continued evolution of gases, which were considered to be decomposition products from the glass itself.

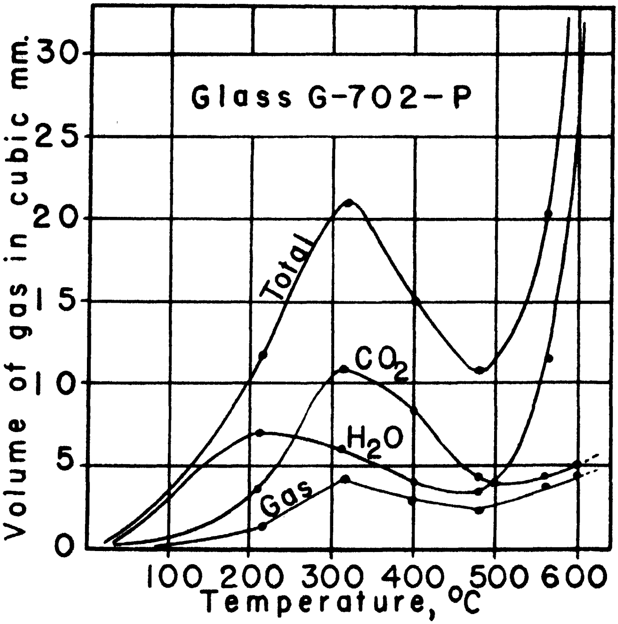

Figure III. 2.—The Rate at which Various Gases are Evolved from Glass on Heating in a Vacuum. After Sherwood.

Sherwood studied the relation between the temperature of treatment and the quantity of gaseous products driven off by a succession of three-hour heat treatments at increasing temperature, with the results shown in Fig. III. 2. The curves for carbon dioxide and permanent gas show maxima a little above 300° C.; the curve for water shows a maximum at about 200° C., and above 500° C. it rises steeply. The maximum in the curve for total gas probably refers almost entirely to adsorbed gas, and the rapid rise above 500° C. probably was caused by the evolution of water dissolved in the glass.

TABLE III. 5—Compositions of Glasses Studied by Harris and Schumacher

	Glass 1	2	3	4	5	6
SiO_2	69.93	69.40	64.64	61.50	72.05	65.47
*B_2O_3	2.36	3.12	0.37	2.27	14.07	
Na_2O	21.02	16.67	9.10	8.14	4.23	6.40
K_2O	0.10	0.20	3.20	3.76	1.12	3.59
MgO	0.03	4.09	0.02	0.36	0.09	0.13
CaO	3.17	5.15	0.02	0.21	0.06	0.22
PbO	1.44	Trace	21.66	22.55	6.11	20.20
MnO	0.09	0.19		0.19	0.01	0.07
Al_2O_3	1.54	0.78	0.20	0.57	2.21	2.99
Fe_2O_3	0.19	0.14	0.04	0.11	0.05	0.51
P_2O_5	0.08	0.16	0.75	0.34	Trace	Trace
Sb_2O_3	0.05	0.10		Trace		

* By difference, Nos. 3 and 5 contain a trace of F; No. 6, 0.013 SO_3; BaO, trace.

Harris and Schumacher[44] studied the evolution of gas from six types of glass, of the compositions given in Table III. 5. The composition and the volume of the gases obtained by heating in vacuum to specified temperatures are in Table III. 6. To determine the relation between adsorbed and absorbed gas, *i. e.*, gas in solution in the outer

TABLE III. 6—Composition of Gases Evolved on Heating in Vacuum the Glasses of Table III. 5

After Harris and Schumacher

Vol. of Sample cc.	Surface Area Sq. Cm.	Temp. to Which Glass Was Heated ° C.	Total Gas Vol. cc.		Comp. of Gas Per cent	Vol. in cc. per Sq. Cm. × 10⁴	Vol. per cc. Glass × 10⁴
37.2	580	400	H_2O	2.70	88.5	46.6	726
			CO_2	0.32	10.5	5.5	86
			*P. G.	0.03	1.0	0.5	8
			Total	3.05	...	52.6	820
31.9	540	400	H_2O	1.62	92.6	30.0	508
			CO_2	0.11	6.3	2.0	34
			P. G.	0.02	1.1	0.4	6
			Total	1.75	...	32.4	548
26.5	565	400	H_2O	1.34	96.4	23.7	506
			CO_2	0.03	2.2	0.5	11
			P. G.	0.02	1.4	0.4	8
			Total	1.39	...	24.6	525
24.1	540	400	H_2O	1.37	97.2	25.4	568
			CO_2	0.02	1.4	0.4	8
			P. G.	0.02	1.4	0.4	8
			Total	1.41	...	26.2	584
25.2	469	500	H_2O	0.03	33.3	0.6	12
			CO_2	0.04	44.5	0.9	16
			P. G.	0.02	22.2	0.4	8
			Total	0.09	...	1.9	36
15.6	292	400	H_2O	0.03	49.6	1.0	19
			CO_2	0.03	49.6	1.0	19
			P. G.	0.0005	0.8	0.02	0.3
			Total	0.0605	...	2.02	38.3

* P. G. indicates permanent gases.

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[44] Harris, J. E., and Schumacher, E. E., *Ind. Eng. Chem.*, **15**, 174 (1923).

layers of the glass samples, the total pressures of the gases evolved were determined at intervals of 100° C. from 100° C. to the softening point of the glass, with the results shown in Fig. III. 3. Glass No. 7 was Pyrex chemical resistant glass. The adsorbed gases from the lime and lead glasses were all given up at 200° C., whereas 300° C. was required for the borosilicate glasses. The absorbed gases began to come off at the softening points of the glasses. When it was manufactured, glass No. 6 had been given a special heat treatment at 1500° to 1600° C. for one hour; and as a result it gave off less gas than other glasses of similar composition. Most of this gas had been adsorbed, as shown by the curve of Fig. III. 3. It was concluded that the amount of adsorbed water and the amount of carbon dioxide increased with increasing content of alkali oxide in the glass.

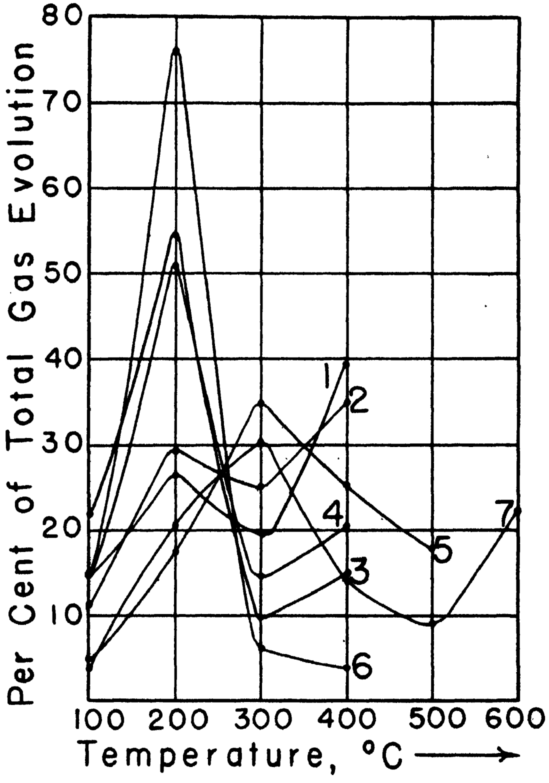

FIGURE III. 3.—Percentage of Total Gas Evolution as a Function of Temperature, from the Glasses of Table III. 6. After Harris and Schumacher.

Dissolved Volatile Substances

The volatile substances found in solution in glass are all components of the original batch: water, in combination as hydroxides or hydrated salts, or as "wet" batch; carbon dioxide, in combination as carbonates; oxygen, in combination as nitrate or introduced mechanically as entrapped air; sulfur dioxide, introduced as sodium sulfate; and nitrogen, from entrapped air. During the melting of the glass, these substances are given off in large quantities; that which remains in the glass is only a small proportion of that introduced into the batch.

Experimental evidence indicates that glass at the melting temperature is approximately in equilibrium with the furnace atmosphere. Dalton[45] found the water content depended on the partial pressure of water vapor in the furnace atmosphere, and he found that small meltings in an electric furnace contained much less water than did large ones made in a gas-fired furnace. The content of carbon dioxide could not be altered by enriching the furnace atmosphere in oxygen. The experiments of Weyl[46] indicated that an ordinary soda-lime glass would not have over one-thousandth of one per cent carbon dioxide in equilibrium with an ordinary furnace atmosphere at 1400° C., an amount equivalent to less than one-half cubic centimeter in 100 grams of glass.

The amount of gas in solution depends on the temperature, the pressure, and the composition of the glass. Niggli,[47] working with melts of sodium or potassium carbonate and silica, in carbon dioxide at one atmosphere pressure, found that the amount in the melt decreased with an increase in the proportion of silica, that is, with more "acid" glasses. When he studied the equilibrium between silica and alkali carbonates, at temperatures above the freezing points of the melts and at one atmosphere pressure of carbon dioxide, Niggli found the amount of CO_2, calculated as alkali carbonate, decreased with the decreasing ratio of alkali oxide to silica. For example, when the ratio was 1:1 (metasilicate) in the system CO_2-K_2O-SiO_2 at 898° C., the melt contained 13.8 mole per cent CO_2; at 956° C., 11.9 mole per cent; when the ratio was 1:2 (disilicate), the CO_2 was completely expelled at each temperature.

Morey and Fenner,[48] working with potassium silicate glasses melted under pressures of water vapor up to and above one hundred atmospheres, found that the amount of water dissolved in the glass increased linearly with increasing pressure, in accordance with Henry's law. The hydrous glasses so obtained were hard and brittle at ordinary temperatures when the water content was small, and passed by a continuous series of stages to thick, sticky liquids as the water content was increased; at the

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[45] Dalton, R. H., *J. Am. Ceram. Soc.*, **16**, 425 (1933).

[46] Weyl, W., *Glastech. Ber.*, **9**, 641 (1932).

[47] Niggli, P., *J. Am. Chem. Soc.*, **35**, 1693 (1913).

[48] Morey, G. W., and Fenner, C. N., *J. Am. Chem. Soc.*, **39**, 1173 (1917).

temperatures of the experiment, they were, of course, fluid solutions. Comparison of the results with a given ratio of K_2O to SiO_2, at constant pressure and changing temperature, indicated that the solubility of water in the melt decreased with increasing temperature, as is usually the case. When hard hydrous glasses were heated quickly, rapid expulsion of the water resulted in the formation of a pumice; sudden heating of an obsidian high in water (Table III. 1) has a similar effect. Möttig and Weyl[49] studied the solution of oxygen by molten glass under pressure. A glass of the composition $PbO \cdot SiO_2$, when melted at 1100° C. under an oxygen pressure of 300 atmospheres, gave no test for plumbate with potassium iodide solution; whereas a glass of the composition $0.25\,K_2O + 0.75\,PbO + 1.0\,SiO_2$ showed six per cent of potassium plumbate, K_4PbO_4, and by heating in vacuum gave off oxygen. A barium glass, of composition $K_2O \cdot BaO \cdot 4SiO_2$, melted under 300 atmospheres pressure of oxygen, showed dissolved oxygen equivalent to eight per cent BaO_2; a soda-barium glass, $Na_2O \cdot BaO \cdot 4SiO_2$, showed six per cent BaO_2.

Experimental Results

The earliest study of gas dissolved in glass was by E. S. Shepherd, cited by Allen and Zies.[50] Analyses by Allen and Zies gave: Na_2O, 10.37%; K_2O, 0.44%; CaO, 14.73%; and SO_3, 0.74%. Shepherd heated 6.577 g. of the glass to 1200° C., pumped out the gases, and passed them through an absorption tube containing silver oxide and potassium carbonate to absorb the SO_2. He obtained 0.0025 g., equivalent to 0.87 cc. under standard conditions. The remaining gases, amounting to 6.55 cc. under standard conditions, gave the following percentages by volume: O_2, 64.2; CO_2, 24.2; CO, 3.5; H_2, 3.9; N_2, 4.1. The SO_2 and some of the O_2 may have come from decomposition of the SO_3. Water was not determined.

TABLE III. 7—Composition of Gases Dissolved in Glass

After Washburn, Footitt, and Bunting

Glass	Volume per cent $t = 0°$ C., $p = 760$ mm. Hg.				Weight per cent				Concentration (Moles per liter)		
	O_2	CO_2	N_2	Total	O_2	CO_2	N_2	Total	O_2	CO_2	N_2
Barium flint, 1	83	27	1	110	0.035	0.011		0.046	0.033	0.011	
Barium flint, 2	36	12	1	48	0.015	0.0045		0.020	0.016	0.005	
Light flint	4.5	10	3	18	0.0045	0.014	0.0025	0.021	0.004	0.010	0.003
Borosilicate crown	6	5	6	17	0.0036	0.010	0.0031	0.010	0.0028	0.002	0.0028

Washburn, Footitt, and Bunting[51] demonstrated the presence of gases in glass by heating a sample to 1200° C. at atmospheric pressure, then quickly evacuating the furnace, whereupon the rapid liberation of

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[49] Möttig, M., and Weyl, W., *Glastech. Ber.*, **11**, 67 (1933).

[50] Allen, E. T., and Zies, E. G., *J. Am. Ceram. Soc.*, **1**, 739 (1918).

[51] Washburn, E. W., Footitt, F. F., and Bunting, E. N., *Univ. Ill. Eng. Expt. Sta. Bull.*, **118** (1920).

gas caused the glass to foam, its volume becoming about six times that of the original piece. An apparatus was devised to analyze the glass, which did not permit determination of the amount of water. The results are summarized in Table III. 7. The barium flint glass had an index of refraction of about 1.605, a ν-value of about 43.6; and probably it did not differ greatly in composition from No. 33, Table III. 4. The two samples studied were not necessarily from the same melt. The "light flint bulb glass" had the following composition in percentages by weight: SiO_2, 62.6; Na_2O, 14.2; CaO, 0.5; PbO, 22.2; Al_2O_3, 0.6.

Salmang and Becker[52] described an apparatus for the extraction under vacuum of the gases in glass. A soda-lime glass, in which the soda was derived from the decomposition of sodium sulfate, frothed so much at 1200° C. that it was not possible to work with one gram of glass even in a crucible 50 mm. × 35 mm. Different meltings of a glass of the percentage composition: SiO_2, 76.4; Na_2O, 15.3; CaO, 8.3, made from carbonate and a little nitrate gave, from 10-gram samples, values of CO_2 ranging from 0.05 cc. to 7 cc., of O_2 from 0.07 cc. to 0.28 cc., and of water, calculated as gas at normal temperature and pressure, from 2.5 cc. to 6.6 cc. Experiments on glasses containing different proportions of the Na_2O introduced as Na_2SO_4 showed that the decomposition of sulfate was not complete, and that the degree of decomposition could be correlated only with the source of the glass, hence with its unknown history.

TABLE III. 8—Composition of Gases Dissolved in Some Optical Glasses

After Becker and Salmang

No.	Total gas	CO_2	O_2	H_2O
A	37.5	22.7	14.2	4.3
B	3.6	0.6	2.3	3.1
C	1.5	0.13	1.3	1.7
D	0.53	0.14	0.37	1.3
E	1.5	0.2	1.27	2.1

Unit: Volume in cc. at normal temperature and pressure obtained from 10 g. of glass.

Becker and Salmang[53] analyzed the gases from five optical glasses of the following percentage compositions: A.—SiO_2, 31.46; B_2O_3, 12.30; BaO, 49.63; Al_2O_3, 6.02; As_2O_3, 0.57. B.—SiO_2, 49.80; B_2O_3, 6.0; Na_2O, 3.92; K_2O, 4.97; BaO, 20.26; ZnO, 11.40; PbO, 3.13; As_2O_3, 0.40. C.—SiO_2, 34.1; Na_2O, 1.5; K_2O, 2.5; PbO, 61.95; As_2O_3, 0.45. D.—SiO_2, 45.07; Na_2O, 1.43; K_2O, 6.91; PbO, 46.29; As_2O_3, 0.3. Glass E was obtained from D by adding three per cent of CeO_2. The average values of five analyses, calculated to cc. for a 10-gram sample, also are given in Table III. 8. The agreement among duplicate determinations is shown

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[52] Salmang, H., and Becker, A., *Glastech. Ber.*, 5, 520 (1928).

[53] Becker, A., and Salmang, H., *Glastech. Ber.*, 7, 241 (1929).

by the following volumes of total gas from A, in cc.: 37.8, 30.3, 44.4, 32.7, 42.3. Glass E foamed strongly in the furnace, and the CeO_2 did not favorably affect the fining.

Experiments were made on glasses containing important amounts of iron oxide, some melted in an electric furnace in air, others in a gas furnace. A glass containing four per cent Fe_2O_3 melted under oxidizing conditions gave off most oxygen, 14.9 cc. per 20 g.; one containing two per cent Fe_2O_3, melted under oxidizing conditions, gave 7.4 cc.; one containing 2 per cent Fe_2O_3, 19 per cent Na_2O, and 9 per cent CaO, melted under reducing conditions, gave off 4.6 cc.; and one containing 2 per cent Fe_2O_3, 9 per cent Na_2O, and 19 per cent CaO, melted under reducing conditions, gave 8.9 cc.

Dalton [54] devised an apparatus for the analysis of the gases including water evolved from glass at 1400° C. Table III. 9 contains the results from the first paper on experimental glasses. The three analyses of gases from glass A refer to samples differently prepared: A.—melted 24 hours at 1350° C. in a 100-pound pot; A′.—melted 16 hours at 1350° C. in a 1-pound clay crucible; and A″.—melted 6 hours at 1350° C. in a 100-gram porcelain crucible in an electric furnace. In spite of the longer heating of the 100-pound melt, it had a content of water almost twice that of the 100-gram melt in an electric furnace, probably because the partial pressure of water vapor above the small melt was much less than in the gas-fired furnace.

TABLE III. 9—Composition of Gases Dissolved in Some Experimental Glasses

After Dalton

Glass	H_2O	CO_2	O + R
A	33	7	2
A′	25	7	2
A″	18.4	6	1
B	33	3	47
C	25	2	13
D	74	1	1

Unit: Volume in cc. at 0° and 1 atm. pressure obtained from 100 g. of glass. R refers to N, or other inert gas.

Glass B was similar in composition to A, but it contained also 0.5 per cent As_2O_3, with enough $NaNO_3$ to oxidize it to As_2O_5; Glass A had a little $NaNO_3$ added to the batch "to fix the state of oxidation." The large increase in the content of oxygen probably resulted from the decomposition of As_2O_5; and this ability to give off oxygen is considered to be the explanation of the value of arsenic oxide as an aid in the "fining" of glass, that is, in freeing the glass from tiny bubbles, or "seed." These bubbles, so small that they would take a long time to

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[54] Dalton, R. H., *J. Am. Ceram. Soc.*, **16**, 425 (1933); *J. Am. Chem. Soc.*, **57**, 2150 (1935).

rise through the glass, serve as nuclei for the liberation of oxygen from As_2O_5, thus increasing the size of the bubbles and hastening their rise through the glass.

Glass C was an example of a glass with about 0.75 per cent Na_2SO_4, "salt cake," added. It gave off 16 cc. of SO_2, which, together with one-half its volume of oxygen, came from the decomposition of SO_3.

Glass D was a borosilicate glass. The higher content of water and the lower content of carbon dioxide is characteristic of the borosilicate glasses.

In the second paper, Dalton[55] described an apparatus for analyzing the gases evolved at 1400° C. from samples of glass of about one gram in weight, that is gas samples from 1.0 to 0.01 cc. Analyses are given (Table III. 10) of the gases from several commercial glasses, and from one experimental glass (No. 8) containing an unusually large amount of arsenic. The third column of the table gives the total gas evolved from one gram of glass, calculated to 0° C. and one atmosphere pressure.

TABLE III. 10—Composition of Gases Obtained from Some Commercial Glasses
After Dalton

			Percentage composition of gases									
No.	Glass type	Gas, cc.	H_2O		SO_2		CO_2		O_2		R	
I	Barium (optical)	0.71	24	22			40	37	36	41	0.1	0.1
II	Soda-lime (milk bottle)	.93	51	51	33	34	3	3	12	11	0.1	0.1
III	Borosilicate (heat resistant)	.40	91	92			5.5	4.5	3.5	3.5		
IV	Soda-lime (bulb)	.90	44	44	35	36	4.5	7	16	13		
V	Borosilicate (heat resistant)	.36	92	89	0.3	0.3	3	4	5	7		
VI	Borosilicate (bulb)	.74	94	94		2.5	3		3	3.5		
VII	Lead (sign tubing)	.70	33	39		8	7		59	54		
VIII	Soda-lime (expt.)	1.41	28	28		10	8		62	64		
IX	Borosilicate (heat resistant)	0.44	93	93		2	4		5	3		

Hahner, Voigt, and Finn[56] described an apparatus for the removal and the analysis of the gases dissolved in glass, which was applied to several optical and commercial glasses, with the results given in Table III. 11. The chief source of error in the analyses came from the absorption of the evolved gases by volatilized oxides condensed on the colder portions of the vacuum furnace. This source of error also had been noticed by Dalton. There was no significant difference in the amounts of gas obtained from samples taken at intervals during the melting process, although the fine bubbles decreased in size and in number during the process. Since the amount of gas obtained from all optical glasses was relatively small in comparison with that obtained from window glass, and since all the glasses except the light barium crown were relatively free from tiny bubbles, it was concluded that there probably is no relation between dissolved gas and the prevalence of seeds in the light barium crown.

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[55] Dalton, R. H., *J. Am. Chem. Soc.*, **57**, 2150 (1935).

[56] Hahner, C., Voigt, G. Q., and Finn, A. N., *J. Research Natl. Bur. Standards*, **19**, 95 (1937) (RP 1014).

TABLE III. 11—Average Values for Volumes of Gases Obtained from Glasses, and Compositions of the Glasses

After Hahner, Voigt and Finn

Optical Glasses

Glass[1]	Temperature of outgassing °C.	ml Gas per 100 g. of glass			Percentage composition of glass[2]												
		H_2O	O_2+R	CO_2+SO_2	SiO_2	B_2O_3	Na_2O	K_2O	CaO	MgO	ZnO	BaO	R_2O_3	As_2O_3	As_2O_5	Sb_2O_3	SO_3
Borosilicate crown *A* (2)	1,325	49	0.2	<0.1	65.6	11.4	7.9	12.8	...	...	1.8	...	...	0.03	0.40	...	...
Borosilicate crown *B* (3)	1,345	29	0	0	65.6	11.4	7.9	12.8	...	...	1.8	...	...	.5	...	...	...
Light barium crown *A* (2)	1,350 1,325	20 31	1.0 .8	0 0	47.1	4.3	1.9	7.7	2.1	...	8.5	27.9	...	.01	.53	...	...
Light barium crown *B* (3)	1,345	21	1.2	.7	46.6	3.7	.5	7.1	...	...	7.8	33.7	...	.6	...	...	...
Light barium crown *C* (2)	1,345	17	1.1	<.1	46.9	3.7	.5	7.1	...	...	7.9	33.2	...	.2	...	0.5	...
Light crown *A* (4)	1,300	33	1.7	4.0	71.0	...	15.4	...	13.1	...	...	...	...	.01	.31	...	...
Light crown *B* (1)	1,350	38	5.4	4.1	71.0	...	15.4	...	13.1	...	...	...	...	.5	...	...	...
Commercial Glasses																	
Window glass *A* (2)	1,345	16	10.2	43.1	72.1	...	13.5	...	10.0	3.3	...	...	0.7	...	...	...	0.35
Window glass *B* (2)	1,345	28	17.1	17.0	72.6	...	15.0	...	8.0	3.6	...	...	.7	...	...	...	.47
Window glass *C* (2)	1,345	22	32.5	26.6	73.1	...	12.4	0.1	13.3	.3	...	...	1.0	...	...	...	.44
Window glass *D* (2)	1,345	26	22.2	51.2	70.9	...	12.2	.1	11.2	4.4	...	...	.9	...	...	...	.41
Window glass *E* (3)	1,345	32	7.9	40.2	71.5	...	15.0	.2	10.6	1.8	...	...	.9	...	...	...	.45
Window glass *F* (2)	1,345	26	3.3	40.4	72.3	...	15.1	.3	10.0	1.0	...	...	.6	...	...	...	.50
Soda-lime tubing[3] (6)	1,345	23	3.0	14.0	...	...	...	...	...	...	...	...	...	...	...	...	.19

[1] The letters in this column indicate separate melts of glass in the optical group and glasses from different factories in the commercial group. The number in parentheses indicates the number of determinations on which the average is based.

[2] The compositions of the commercial glasses were determined by routine analysis. The compositions of the optical glasses were calculated from the batch composition except for the oxides of arsenic when values are given for both As_2O_5 and As_2O_3. In these cases the arsenic was determined analytically. The batch materials used in making the optical glasses were practically free from sulfur compounds.

[3] Not analyzed except for SO_3.

Permeability of Glass to Gases

Observations made over a period of years have shown that some glasses are permeable to some gases, especially at high temperatures. Silica glass appears to be the most permeable, and helium the gas which diffuses most readily.

Villard[57] was the first to notice that helium diffuses through silica glass at a red heat. Jaquerod and Perrod[58] found that the helium thermometer could not be used at high temperatures because of the permeability of silica glass. Richardson and Ditto[59] found that neon also diffuses through silica glass tubes, but at a slower rate than helium. Bodenstein and Kranendieck[60] found that silica glass was permeable to hydrogen, with a doubling of the rate in the temperature interval from 732 to 880° C.

Mayer[61] found no indication of permeability to hydrogen or oxygen in the case of Jena glass up to 800° C., or of silica glass at room temperature. No permeability of silica glass to oxygen at atmospheric pressure was found up to 690° C., but with pressure differences ranging from 20 cm. of mercury above and below atmospheric pressure, some diffusion was found, increasing with increase of pressure and of temperature. Similar results were obtained with hydrogen and nitrogen; with hydrogen, some diffusion was observed at atmospheric pressure, and with nitrogen, diffusion was not found below 4330° C.

According to Williams and Ferguson[62] the permeability of modern water-clear silica glass can hardly be predicted from the results of the earlier experimenters. They could find no indication that evacuated tubes of either "Pyrex" or Jena combustion glass were permeable to hydrogen at one atmosphere pressure up to 640° C., or that a silica glass tube was permeable to air or nitrogen at one atmosphere pressure up to 640° C. "Pyrex" glass was found to be permeable to helium at 610° C. Silica glass became appreciably permeable to hydrogen at 300° C., and in experiments at several pressures and at temperatures up to 881° C., the amount of diffusion was found to increase linearly with pressure and exponentially with temperature. The permeability of silica glass to helium became appreciable at 188° C., and at 500° C. silica glass was about 22 times as permeable to helium as to hydrogen.

Elsey[63] found that silica glass was permeable to helium at room temperature at a pressure of 1000 atmospheres, but he could find no indication of permeability to hydrogen under the same conditions.

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[57] Villard, P., *Compt. rend.*, 130, 172 (1900).

[58] Jaquerod, A., and Perrod, L. F., *Compt. rend.*, 140, 1542 (1905).

[59] Richardson, D. W., and Ditto, R. C., *Phil. Mag.*, 22, 794 (1911).

[60] Bodenstein, M., and Kranendieck, F., *Nernst Festschrift*, 100, Halle (1912).

[61] Mayer, E. C., *Phys. Rev.*, 6, 283 (1915).

[62] Williams, G. A., and Ferguson, J. B., *J. Am. Chem. Soc.*, 44, 2160 (1922).

[63] Elsey, H. M., *J. Am. Chem. Soc.*, 48, 1600 (1926).

Chapter IV

The Chemical Durability of Glass

The resistance which glass offers to the corroding action of water, of atmospheric agencies (primarily water and carbon dioxide), and of aqueous solutions of acids, bases and salts is a property of great practical significance, and is denoted by the term "chemical durability." In a large proportion of the uses to which glass is put, its power of resisting such attack is the chief reason for its preference over competing materials. An example is the use of glass containers, of which enormous numbers are used for the distribution of commodities ranging from milk to medicine and acids. In this field the superiority of glass leaves it without a competitor. Even in chemical manufacturing, where the requirements are more exacting, glass is being used to an increasing extent as an engineering material because of the resistance which it offers to surface attack under extreme conditions. In other uses of glass, chemical durability is a secondary factor; the requirement of a chemical durability sufficient for the service contemplated places a limit on the compositions which may be employed. Examples of such uses are those in which glass is chosen for its optical properties, uses ranging from windows to lens systems. Although glass used for such purposes is not subjected to as drastic treatment as in the preceding cases, nevertheless it is essential that there be no appreciable amount of surface alteration.

So important is this property of withstanding corroding agencies that Zschimmer[1] included such resistance in his definition of glass. While such a definition seems too restrictive, the necessity of producing glass stable enough to serve the purpose for which it is intended places a practical limit on the compositions which may be employed. The limit set by this requirement differs widely with the use for which the glass is intended. Many glasses possessing desirable optical or mechanical properties are unsuitable because of their susceptibility to corrosion; others may be suitable for optical purposes in protected lens systems and still be worthless for laboratory use. The methods of testing glass thus become of fundamental importance.

Theoretical Discussion

Before considering the testing methods in use, it will be well to con-

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[1] Zschimmer, E., in Doelter, C., "Handbuch der Mineralchemie," 1, 855, T. Steinkopff, Dresden u. Leipzig, 1912.

sider the nature of the processes involved in the decomposition of glass by water.[2] It is not a simple case of solution, and the testing of glass is not merely the determination of its solubility in water. On the contrary, the process is a highly complex one, involving the penetration of the glass by water and the subsequent decomposition of the complex silicate mixture, with formation of substances wholly different

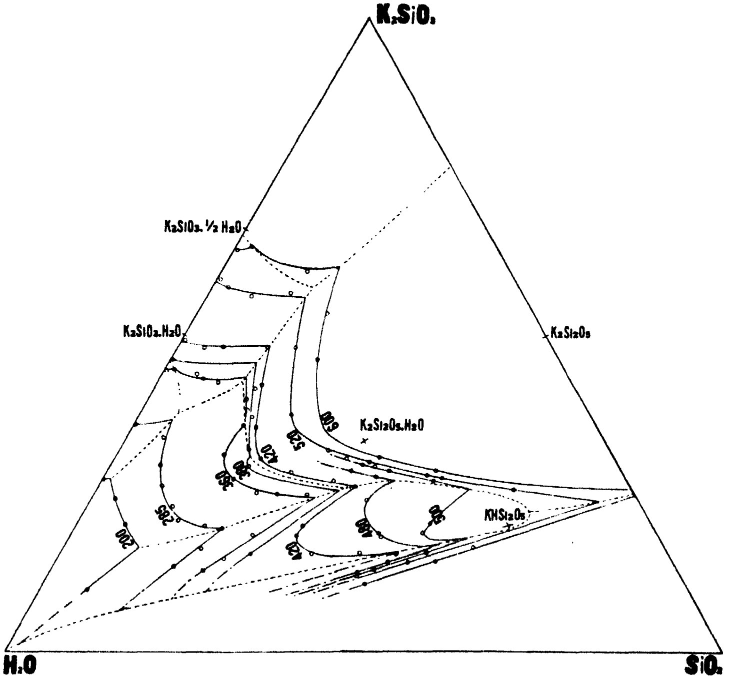

FIGURE IV. 1.—Isothermal Polybaric Saturation Curves in the System H_2O-K_2SiO_3-SiO_2. After Morey and Fenner.

from those originally present. The distinction between the processes of true solubility and of decomposition is so fundamental to the consideration of the effect of water on glasses that a brief consideration of this subject from the point of view of the phase rule will prove of value.

In a system composed of water and a salt which is not decomposed by water, the "solubility" of the salt in water has a definite meaning. Coexistence of three phases—solid, solution and vapor—in a system of two components—water and salt—leaves but one degree of freedom; so that fixing any one of the variables—temperature, vapor pressure of the solution or composition of the solution—fixes the other two. This is

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[2] Compare Morey, G. W., and Fenner, C. N., *J. Am. Chem. Soc.*, **39**, 1173-1229 (1917); Morey, G. W., *J. Soc. Glass Tech.*, **6**, 20-9 (1922); Morey, G. W., *Ind. Eng. Chem.*, **17**, 389 (1925).

not necessarily true of systems in general; and the actual reaction which takes place between water and a multi-component system such as glass may be different indeed. As an illustration of such a case the system H_2O-K_2SiO_3-SiO_2 may be chosen. This has been studied[8] over the range from 180° to 1000° and under pressures ranging from one to several hundred atmospheres. The results of this investigation are summarized in Fig. IV. 1 which gives a number of isotherms in the system, as well as boundary curves, shown as broken lines.

Along each of the several portions of an isotherm, a single solid phase is stable in contact with a liquid of continuously changing composition and with a vapor of continuously changing pressure. At 285°, for example, there are three distinct saturation curves: those of potassium metasilicate monohydrate, $K_2O \cdot SiO_2 \cdot H_2O$; of potassium disilicate monohydrate, $K_2O \cdot 2SiO_2 \cdot H_2O$; and of potassium tetrasilicate monohydrate, $K_2O \cdot 4SiO_2 \cdot H_2O$. There is also a saturation curve of quartz, SiO_2, at this temperature, as there is at higher temperatures, but it was not determined. The solubility of potassium metasilicate monohydrate in water is given by the end-point of the metasilicate curve on the H_2O-K_2SiO_3 side of the diagram; and on increasing the ratio SiO_2/K_2O in the liquid, the solution follows the saturation curve of the metasilicate until this is intersected by the saturation curve of the disilicate monohydrate. The disilicate then becomes the solid phase, and remains so until its saturation curve is intersected by that of the tetrasilicate monohydrate at a SiO_2/K_2O ratio a little greater than two. With further increase in SiO_2, the tetrasilicate monohydrate remains the stable phase until quartz makes its appearance, at the invariant point SiO_2-$K_2O \cdot 4SiO_2 \cdot H_2O$-solution-vapor.

At 285°, when H_2O is added to anhydrous $K_2O \cdot SiO_2$ or to a glass of that composition, some is dissolved and the rest remains as the crystalline monohydrate. A similar result is obtained when H_2O is added to $K_2O \cdot 2SiO_2$. At 285°, therefore, both the metasilicate and the disilicate have a definite solubility in water. As more and more water is added in either case, more and more of the solid phase passes into solution; but the composition both of the solid and of the liquid remains the same throughout the process. At 200° a very different condition exists as regards the disilicate. Starting at the metasilicate side of the diagram, we find that the metasilicate still has a definite solubility, and on increasing the SiO_2/K_2O ratio the solution follows the saturation curve of the metasilicate until it is intersected by the saturation curve of the disilicate. This saturation curve gives the composition of the solutions which can exist in equilibrium with the disilicate at 200°; and these solutions are terminated by the invariant point $K_2O \cdot 2SiO_2$-$K_2O \cdot 4SiO_2 \cdot H_2O$-solution-vapor. At 285°, the solution at this intersection has a

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[8] Morey, G. W., and Fenner, C. N., *J. Am. Chem. Soc.*, **39**, 1173 (1917).

SiO_2/K_2O ratio of greater than two; at 200° the ratio is less than two. In other words, at 285° the invariant solution is on the SiO_2 side of the tie-line H_2O-$K_2O \cdot 2SiO_2$; at 200°, on the $K_2O \cdot SiO_2$ side. When H_2O is added to $K_2O \cdot 2SiO_2$ at 285°, enough disilicate is dissolved to give a saturated solution in which the SiO_2/K_2O ratio is the same as in the solid phase, and the only effect of adding more H_2O is to change the amount of the liquid, the composition of both the solid and liquid phases remaining constant. When H_2O is added to $K_2O \cdot 2SiO_2$ at 200°, the result depends on the amount of water added. If the amount is small, most of the solid will remain as $K_2O \cdot 2SiO_2 \cdot H_2O$; but some of the latter will be decomposed to give the extra K_2O required for the invariant solution, and the resulting excess SiO_2 will appear as $K_2O \cdot 4SiO_2 \cdot H_2O$. As more water is added, more solution will be formed, more $K_2O \cdot 2SiO_2 \cdot H_2O$ decomposed, and more $K_2O \cdot 4SiO_2 \cdot H_2O$ formed; the proportion of the two crystalline phases, and hence the gross composition of the solid material, changes continuously until all the disilicate has disappeared. In contrast to the true solubility of disilicate shown at 285°, we have here decomposition by water, and it is evident that at this temperature the disilicate can not be said to possess a true solubility in water.

At a slightly lower temperature the metasilicate also is decomposed by water, and from the shape of the isotherms it is probable that at room temperature all compounds of potash and silica are so decomposed. True equilibrium at ordinary temperatures in any mixture, no matter how alkaline, probably would mean a solution containing a vanishingly small amount either of quartz or of a crystalline compound of SiO_2 and H_2O, if any such exists. The end result of treating potassium disilicate with water at ordinary temperatures, if the peptization of the silica could be prevented and true equilibrium attained, would be that practically all the SiO_2 would be left as quartz, and the liquid would consist of a solution of KOH containing a small amount of dissolved silica. But this solution would in no sense represent the solubility of potassium disilicate in water.

This system is analogous to those obtained with complex silicates such as glasses and ceramic bodies and glazes, as well as natural minerals. When such substances are treated with water, either at ordinary temperatures or at such moderate temperatures as are obtainable in autoclaves, they are decomposed, just as the potassium silicates are decomposed, and more or less of certain constituents pass into solution. In all these cases, the end result, if equilibrium were attained, would be an alkaline liquid, containing small amounts of certain constituents, and vanishingly small amounts of others, together with various crystalline phases, depending on the complexity of the original material. But the composition of this liquid would have no bearing on the "solubility" of the substance which had been decomposed, for the term "solubility" has no meaning in such a case. The original state of the material, whether it be crystalline or glassy, or a mixture of the two, will have no bearing on the end result of such a decomposition; although it will affect the rate of decomposition, and therefore will affect the results observed in any experiment not carried to its ultimate conclusion.

The preceding discussion has dealt with the action of water alone, but frequently the resistivity of glass to the action of aqueous solutions is of importance. In many cases, the solutions are dilute enough so that the differences caused by the dissolved material are not significant, but this is not always true. Whether or not such substances are present, the action will tend to go on until decomposition of the glass is complete. The presence of an acid or alkali often will profoundly affect the rate of decomposition, which is the subject in which we are primarily interested, and the effect will be dependent both on the composition of the glass and on the dissolved material. Decomposition of most glasses by water results in the liberation of alkali, by the process just outlined for the potassium silicates, and the liberated alkali may accelerate the further decomposition of the glass. For this reason, some types of glass, notably those containing a high percentage of silica and boric oxide, are more resistant to acid solutions than to water, and more resistant to water than to alkalies. On the other hand, glasses containing a low percentage of silica usually are more rapidly attacked by acid solutions: indeed, wollastonite glass ($CaO \cdot SiO_2$) and extra heavy lead or barium glasses can be decomposed rapidly enough for analytical purposes by digesting them with hydrochloric or with nitric acid. The action of concentrated solutions of salts and acids often is in harmony with the views of Foerster,[4] who assumed that the acids exert no direct action on the glass, and that the attack is due exclusively to water. This view leads naturally to the conclusion that a large amount of acid weakens the attack by diminishing the concentration of water, a conclusion borne out by his experimental results.

It is evident, then, that the term "solubility" has no meaning in such a case, and there can be no quantitative figure for the solubility of the simplest glass in water. All that can be measured and compared is a rate of attack; and all the measurements which have been made represent not solubilities, but rates of reaction. Rates of reaction, however, differ from equilibrium values in being highly susceptible to slight differences in experimental conditions and, unfortunately, many of the data in the literature relative to the susceptibility of glasses to attack by reagents have been obtained under poorly defined experimental conditions. Comparison of the results of one observer with those of another is rarely possible, and in any case the validity of such a

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[4] Foerster, F., *Z. Instrumentenk.*, **13**, 457 (1893).

comparison requires proof. Much of the information in the literature is inherently worthless.

Experimental Methods

Since it is not possible to measure definite solubilities of glasses, the suitability of a glass for a particular purpose is best determined by actual service, or by exposing the glass to conditions simulating as nearly as possible those that will be met in service. Thus, for optical glasses, actual use in the finished instrument is the ultimate criterion, and exposure to the elements under service conditions probably the next best test. Such tests require a long time and, in addition, they lack one prime requisite of a test of practical value in the development of resistant glasses. This requisite is that the test shall give such quantitative information that the glass-maker can have a categorical answer to the questions: whether or not a given change in composition or treatment is beneficial, and which of several possible changes is the one which will give the most useful glass. It is in the attempt to provide such a method that much of the information we have on the chemical properties of glasses has been obtained.

Most of the methods that have been used for testing the weathering qualities of glass are variants of a few chief ones. All have been developed from the same basic thesis, namely, that the verdict of actual service may be anticipated by accelerating the corrosive action by the use of drastic reagents, by increasing the surface through the use of powders, or by the use of higher temperatures, and by using sensitive methods to detect and measure the resulting action. Several of these methods have been combined in many cases, for each has its faults as well as its virtues, and no one method can be safely chosen as the test to be applied universally to all kinds of glass. The methods have been discussed critically by Turner and his collaborators,[5] by Haigh,[6] and by Rexer.[7] Turner published an annotated bibliography[8] of the subject, and a summary[9] of experimental results previously presented.

The choice of method is determined largely by the use to which the glass is to be put. Methods suitable for differentiating glasses to be used in optical instruments may be far too mild to discriminate adequately between types of chemical glassware. Thus, exposure to moist air would show no effect on either Pyrex chemical resistant glass or on Jena Geräte glass, but it affords a valuable method for studying

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[5] Cauwood, J. D., English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **1**, 153-202 (1917). Turner, W. E. S., *Ibid.*, **6**, 30-45 (1922).

[6] Haigh, T., "Durability of Optical Glass"; London, British Scientific Instrument Research Association, 1921.

[7] Rexer, E., *Keram. Rundschau*, **38**, 387 (1930).

[8] Turner, W. E. S., *J. Soc. Glass Tech.*, **1**, 213-222 (1917).

[9] Turner, W. E. S., "Chemical Durability of Glasses," Int. Critical Tables, **2**, 107, McGraw-Hill, New York, 1927.

TABLE IV. 1A—Results of "Dimming" Test (30 Hours at 80°) and Iodoeosine Values of Glasses in Table IV. 1B

After Elsden, Roberts and Jones

	Appearance of polished surface at conclusion of "dimming" test					Iodoeosine value, mg. per 100 sq. cm.	
	To unaided eye						
		After removal from tube D					
Glass	In tube D	Dew disappeared in	Surface after disappearance of dew	Under microscope ⅔ in. objective	Classification by dimming test	On freshly broken surface	On broken surface after "weathering" for 7 days at 18°
A	"Dewed"	30 min.	Uniformly "filmed"	Uniform very finely granulated appearance, together with definite drops of liquid irregularly distributed over the surface.	3	0.30	2.21
B	"	15 min.	Distinctly "filmed" more marked at one end of plate	Very finely granulated surface, especially marked at one end of plate. One area of well-defined drops of liquid.	3	0.39	0.60
C	"	1 hour	Heavily "filmed" no longer transparent	Covered with deposit of crystalline appearance, many fern-like clusters, and irregular accumulations of smaller crystalline particles with nuclei of larger ones.	3	0.39	0.37
D	"	20 min.	Distinctly "filmed"	Strongly corroded areas of granular appearance, fern-like clusters, and numerous drops of liquid.	2+	0.16	0.25
E	"	10 min.	Slightly "filmed"	Slightly granulated over whole surface. Some definite drops of liquid.	1+	0.13	0.11
F	"	5 min.	Little affected	A few finely granulated areas, and clusters of minute drops of liquid.	1+	0.13	0.14
G	"	3 min.	Decidedly corroded, no longer transparent	Strongly corroded. surface had marked crystalline appearance. numerous fern-like clusters, no drops of liquid.	3	0.21	0.31
H	"	1 min.	Decidedly "filmed"	Whole surface slightly granulated, many lines of marked corrosion. and concentric areas of crystalline appearance.	2+	0.66	0.97
I	No dew		Very slight "film" over about one quarter of area	The slightly filmed portion of surface showed a few slightly granulated areas. No drops of liquid. Rest of surface unaffected.	1	0.02	0.04
J	"		Uniformly "filmed"	Uniform very finely granulated appearance, small drops of liquid in lines and clusters.	2	0.35	0.36
K	"		Small "filmed" areas, mainly unaffected	The filmed areas showed a finely granulated appearance, rest of surface unaffected.	1+	0.13	0.13

optical glass. This method was employed by Zschimmer,[10] by Mylius,[11] and by Elsden, Roberts, and Jones[12] in their "dimming" test.

In the dimming test, which probably is the most carefully worked out of the methods of this type, the cleaned and polished glass surfaces are exposed to the action of purified water-saturated air at 80° for 30 hours. According to the appearance of the samples, both to the unaided eye and under moderate magnification, the glasses are classified as:

Class *1*. Unaffected, or only slightly affected.
Class *2*. Decidedly affected.
Class *3*. Very seriously affected.

TABLE IV. 1B—Compositions of the Glasses of Table IV. 1A

Glass Ref.	Chemical type	SiO_2	Na_2O	K_2O	MgO	CaO	BaO	PbO	ZnO	Al_2O_3	Reputation, etc.
A	Lime-soda-potash silicate	73.03	12.24	4.38	0.53	6.91	...	...	...	0.74	Very poor.
B	Lime-soda-silicate.	74.63	14.51	...	0.11	6.95	...	0.07	0.39	3.19	Very poor.
C	Lime-soda-silicate.	73.83	16.59	0.21	0.15	7.08	...	...	...	1.73	Very poor.
D	Lime-soda-potash silicate	73.82	13.21	3.77	0.27	7.16	...	0.12	...	1.43	Very poor.
E	Lime-soda-potash silicate	71.31	6.70	10.31	0.23	10.08	...	...	...	1.39	Fair.
F	Lime-soda-silicate.	71.70	13.64	0.99	0.29	11.41	...	...	...	1.92	Fair.
G	Baryta-soda-silicate	67.02	17.35	1.40	0.35	0.86	9.88	...	2.01	0.70	Very poor.
H	Lead-soda-potash silicate	65.24	13.53	4.53	0.36	0.57	...	12.00	2.16	1.45	Very poor.
I	Baryta-soda-borosilicate	68.22	13.34	2.89	0.32	0.60	3.19	...	...	1.33	Good.
J	Lead potash silicate	43.09	2.22	9.89	...	...	...	43.52	...	0.80	Doubtful.
K	Barium-lead-zinc-potash silicate ..	56.65	2.04	11.93	...	...	14.75	10.28	4.01	0.38	Good.

Further classification is afforded by adding the sign "+" or "−," indicating that the glass in question was rather more or less affected than the general standard of the class. Table IV. 1A contains the results obtained by Elsden, Roberts, and Jones, and Table IV. 3 contains the results obtained by Haigh. Both tables include comparisons of the "dimming" method with other methods of testing chemical durability.

Weber[13] was one of the first to study the weathering properties of glasses by means of accelerated tests. He exposed the test pieces to the action of the strongly acid vapors arising from concentrated HCl solutions, and classified the glass qualitatively from the appearance and the intensity of the resulting films. The method is a convenient one for rough work, affording a rapid separation of the poor from the good glasses, but it is not suitable for nice discrimination.

A method of testing which has been applied extensively to optical glass is the iodeosine method of Mylius,[14] the basis of the hydrolytic

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[10] Zschimmer, E., *Z. Elektrochem.*, **11**, 629 (1905); *Deut. Mechaniker-Ztg.*, **7**, 53 (1903).

[11] Mylius, F., *Z. anorg. Chem.*, **55**, 233 (1907); **67**, 200 (1910).

[12] Elsden, A. V., Roberts, O., and Jones, H. S., *J. Soc. Glass Tech.*, **3**, 52-69 (1919).

[13] Weber, R., *Dinglers Polytech. J.*, **171**, 129 (1863); *Ann. Physik Chem.*, **6**, 431 (1879).

[14] Mylius, F., *Z. Instrumentenk.*, **8**, 267 (1888); *Z. anorg. Chem.*, **55**, 233 (1907); *ibid.*, **67**, 200 (1910); *Silikat-Z.*, **1**, 2, 25, 45 (1913). Bichowsky, F. R. v., *J. Am. Ceram. Soc.*, **3**, 296 (1920).

classification adopted in the catalogs of several manufacturers. In this method, a surface of known area is immersed in a solution of iodeosine in ether for one minute, the excess iodeosine is rinsed off with ether, the alkali salt of the dye is dissolved in water, and the amount of iodeosine combined with the alkali is estimated colorimetrically by comparison with a standard solution.

Commercial iodeosine should be purified by recrystallization of the sodium salt from alcohol, or by dissolving it in a slight excess of sodium hydroxide solution, precipitating it with dilute H_2SO_4, and washing it with water. Two or three such treatments will be enough. About 0.5 gram of the purified iodeosine is dissolved in a liter of ether, which has been freed from acid products of decomposition by repeated shakings with Na_2CO_3 solution and washing with water. This solution is sufficiently sensitive when freshly prepared, but deteriorates on standing. It is best to keep a portion of it in contact with a few cc. of one per cent Na_2CO_3 solution, always using from this sensitive stock, and refilling from the main portion. Both solutions should be kept in a cool place in the dark, and preferably in dark bottles. The standard comparison solution contains 0.0106 gram of the purified sodium compound in a liter of neutral water, or 0.01 mg. iodeosine per cubic centimeter. This solution must be kept in dark bottles, protected from the light; and even when so kept, it should be renewed frequently.

The test piece is made most easily from a slab of polished glass, 3 cm. square, and from 5 to 10 mm. thick. The method of breaking described by Mylius is probably best; one edge is notched with a file, the piece is clamped in a vise having cork-lined jaws, the projecting portions are grasped in a parallel-jawed pliers (also cork-lined), and the glass is broken by steady pressure. In this manner a fairly plane fractured surface may be obtained, without splintered edges, the area of which is easy to measure. Scratching with a diamond does not give as good results. The fracture surface is immersed in the ethereal iodeosine solution contained in a flat-bottomed silica dish and moved to and fro for exactly one minute; then it is rinsed in dry neutral ether, to remove excess dye. The adjacent sides are wiped with a damp cloth, taking especial care to remove all the dye from the file mark. All the old surfaces now have been cleaned, and there remains only the fresh surface stained red by the iodeosine combined with the alkali of the glass surface. This is washed off with the minimum quantity of 0.1 per cent sodium carbonate solution, and the amount of iodeosine is determined colorimetrically, using the standard solution described above. The results are expressed as milligrams iodeosine adsorbed per square decimeter of surface; *i. e.*, the number of cubic centimeters of standard solution used, multiplied by one hundred and divided by the area of the fracture in square centimeters. In case the glass to be tested can not be obtained in polished slabs, fresh surfaces should be broken as nearly plane as possible, and the area determined in the manner described by Haigh.[6] After having been washed with carbonate solution, the fractured surface is pressed on an inked pad, and impressions are taken on double paper laid on resilient material. By holding both sheets and by cutting around the stamping, an inkless copy of the tested area is procured. This is weighed, and the area is obtained by calculation from the known weight of the paper.

Mylius distinguished between two kinds of alkalinity, that of the freshly broken surface, and that of the surface after standing in a closed space over water at 18° for seven days. It is well to determine both. When a piece of suitable size is available, it should be quartered, two pieces used for the fresh alkalinity, and two for weathered alkalinity. With the better grades of glass the difference is slight, and the iodeosine value increases on weathering in this manner. The weathered alkalinity is the basis of the hydrolytic classification of glasses devised by Mylius, and widely adopted. Depending on the iodeosine value obtained after exposing freshly fractured surfaces to moist air at 18° for seven days, the glasses are divided into five classes as follows:

Class	Iodeosine per sq. dec.
h^1	0.00 to 0.05 mg.
h^2	0.05 to 0.10 mg.
h^3	0.10 to 0.20 mg.
h^4	0.20 to 0.40 mg.
h^5	0.40 to 0.80 mg.

The iodeosine method is one of the best for testing the chemical resistivity of glass, and gives reliable indications with the common types, in which a lack of stability is associated with an excess of alkali. With other types, however, it may be misleading; BaO, ZnO, or PbO may be present in harmful amounts, and yet fail to be revealed because of the insolubility of their iodeosine compounds in water; and also B_2O_3 does not form a compound. It is important that the details of experimental procedure be closely adhered to, and that the solutions be kept at full strength. The influence of contact with laboratory air and of duration of immersion was shown by Mylius; a certain glass, which had been broken, and, after the indicated treatment, had been immersed for the given periods, gave the iodeosine values of Table IV. 2. Table IV. 1A contains a comparison of the results obtained by the "dimming" and by the iodeosine methods, and Table IV. 3 contains the results of a comprehensive, comparative study by Haigh[6] of several methods of testing optical glass, including the dimming and the iodeosine methods. Rexer[7] considered the iodeosine method the best for general testing of the durability of glass.

Another method of testing glass, the evaporation method, consists of heating it with water or an aqueous solution at atmospheric pressure. This method is applicable particularly to testing chemical glassware, and it has been used repeatedly for that purpose. The chief variations in the method are in the choice of solutions and in the way the extent of the attack is estimated. The cleaned and weighed samples (usually beakers or flasks) are filled to a definite level with the testing solution, and are boiled for a definite time, during which the water lost by evaporation is replaced at frequent intervals, or else is condensed with a reflux condenser. After having been boiled for the requisite time, the samples are rinsed, dried and weighed. The solution may also be tested by a complete analysis, by evaporating to dryness and weighing the residue, or merely by determining the liberated alkali by titration. The usual method is to classify the glasses according to their loss in weight. This method had been used by Walker and Smither,[15] by Nicolardot,[16] and by Turner and his colleagues[17]; although the last investigators determined also the alkali dissolved by titration, and Nicolardot weighed the residues obtained by evaporation of the solution. The evaporation method is not applicable if the alkalinity of the solution is to be determined, nor if the corroding agent is a solution of a non-volatile substance. There is no doubt that the results obtained by the complete analysis of the solution are unexceptionable; but such a determination is laborious, and the additional information gained from it is rarely worth the labor.

TABLE IV. 2—Effect of Treatment After Fracture on the Iodoeosine Value

After Mylius

Treatment after fracture	Immersion period	Iodoeosine value
Immediately immersed in iodoeosine	1 second	0.155
Immediately immersed in iodoeosine	1 minute	0.194
Immediately immersed in iodoeosine	1 minute	0.189
Immediately immersed in iodoeosine	1 minute	0.205
Immediately immersed in iodoeosine	1 hour	0.21
Immediately immersed in iodoeosine	1 day	0.28
Between watch glasses 15 min. before immersion	1 minute	0.195
Exposed to laboratory air 15 min. before immersion	1 minute	0.145
Exposed to laboratory air 1 hour before immersion	1 minute	0.07
Exposed to laboratory air 1 day before immersion	1 minute	0.00
Washed with alcohol, then ether before immersion	1 minute	0.21
Washed with water, alcohol and ether before immersion	1 minute	0.08
10 minutes in water, washed with alcohol and ether before immersion	1 minute	

A similar method has been adopted by the Society of Glass Tech-

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[15] Walker, P. H., and Smither, F. W., *Bureau of Standards Technologic Paper*, No. 107 (1918).

[16] Nicolardot, P., *Compt. rend.*, **163**, 355 (1916).

[17] Cauwood, J. D., English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **1**, 153-202 (1917); Cauwood, J. D., and Turner, W. E. S., *ibid.*, **2**, 219-35 (1918); *ibid.*, **2**, 235-9 (1918); Muirhead, C. M. M., and Turner, W. E. S., *ibid.*, **3**, 129-31 (1919).

TABLE IV. 3—Comparison of Several Methods of Testing the Chemical Durability of Optical Glass

After Haigh

			Hundredths-milligrams of iodoeosine per 100 cm² surface													
			Fractured surfaces					Polished surfaces			Water for 4 hr. at 4 atm.				mg H_2O retained per 100 g. glass powder, 90–100 mesh	
No.	Type	n_D	Fresh	7 da. in moist air at 18°	Fractured under the soln.	Steamed 1 hr. at 2 atm.	Grade	Fresh	7 da. in moist air at 18°	Heated 4 hr. at 150°	Steamed 1 hr. at 2 atm.	Loss in wt. mg/100 cm²	Iodoeosine value of water extract	Grade by appearance	Grade by dimming test	Dried in vacuo	Heated to 120° C.
O/1	Fluor crown	1.4942	3	2	23		h^1	2	2	3		127	182	5			
2	Borosil. crown	1.5108	11	7	10	108	h^2	2	3	4	63	16.6	25.8	3	2	33	0
3	Borosil. crown	1.5135	8	3	18	106	h^1	3	3	4	65	14.8	43.8	1			
4	Borosil. crown	1.5171	17	8	17	112	h^2	2	2	3	72	10.9	41.3	1			
5	Hard crown	1.5173	16	7	8	181	h^2	4	6	9	155	16.9	38.6	1	2—	135	87
6	Soft crown	1.5225	19	69	33		h^5	8	26	23			1875	5	3—	230	151
7	Light Ba crown....	1.5408	14	5	16	150	h^1	3	2	3	108	21.7	38.0	3	1	9	0
8	Medium Ba crown.	1.5736	8	3	12	94	h^1	4	4	3	94	10.5	31.4	3	1+	26	7
9	Dense Ba crown....	1.6129	21	8	22	115	h^2	4	3	3	84	14.0	31.0	1	1+	26	7
10	Dense Ba crown....	1.6111	19	6	21	71	h^3	3	3	3	47	11.5	19.7	4	2—	27	13
11	Dense Ba crown....	1.6052	15	3	19	65	h^1	4	2	4	45	9.8	30.8	4			
12	Telescope flint	1.5177	10	6	11	137	h^2	5	2	4	122	8.6	21.9	4	2—	71	36
13	Light Ba flint......	1.5655	10	3	13	55	h^1	4	4	3	37	9.2	20.9	4	1+	28	12
14	Light Ba flint......	1.5804	14	8	16	130	h^3	5	3	4	126	8.5	18.9	4	2—	53	17
15	Light Ba flint......	1.5282	10	2	11	164	h^1	4	2	3	140	5.8	30.0	2			
16	Ba flint	1.6051	16	2	19	56	h^1	3	2	3	55	6.1	11.5	3			
17	Extra-light flint ...	1.5516	12	8	14	108	h^2	3	4	4	99	2.7	15.5	2			
18	Light flint	1.5741	8	4	10	106	h^1	2	2	3	100	3.7	10.4	2			
19	Light flint	1.5677	11	6	12	95	h^3	3	2	2	89	3.2	8.5	1	1	43	27
20	Dense flint	1.6174	24	6	20	86	h^3	3	2	2	85	4.7	4.2	2	1+	28	16

21	Dense flint	1.6229	21	2	19	85	h^1	3	2	3	80	3.2	3.4	2
22	Extra-dense flint ...	1.6521	26	1	20	69	h^1	2	1	1	58	4.8	6.3	2
23	Borosil. crown	1.5089	12	8			h^2					27.2	73.2	2
24	Hard crown	1.5186	19	9			h^2					17.3	61.7	2
25	Zinc crown	1.5160	11	5			h^1					13.7	31.7	4
26	Light Ba crown....	1.5040	22	3			h^1					18.8	48.0	4
27	Medium Ba crown.	1.5724	11	4			h^1					11.0	31.7	3
28	Dense Ba crown....	1.6087	24	9			h^2					8.4	24.9	3
29	Dense Ba crown....	1.6118	13	6			h^2					9.2	20.7	3
30	Dense Ba crown....	1.6129	14	5			h^1					9.0	28.9	1
31	Light Ba flint	1.5515	12	2			h^1					5.3	18.5	2
32	Dense Ba flint	1.6256	18	2			h^1					2.6	3.5	3
33	Dense Ba flint	1.6683	19	2			h^1					2.8	4.3	3
34	Extra-light flint	1.5280	11	6			h^2					3.5	19.6	4
35	Light flint	1.5789	17	2			h^1					2.4	7.7	1
36	Dense flint	1.6039	19	6			h^2					3.8	6.1	2
37	Dense flint	1.6221	20	4			h^1					2.7	2.7	1
38	Extra-dense flint ..	1.6475	20	2			h^1					4.0	5.2	2
39	Densest extra-large flint	1.7072	14	1			h^1					1.3	1.6	1
40	Fluor crown	1.4933	4	2	4		h^1	2	3	3		513	545	5
41	Borosil. crown	1.5100	17	8	17	107	h^2	3	4	4	87	21.6	63.6	3
42	Silicate crown......	1.5144	28	20	34		h^3	4	17	18		18.2	68.5	4
43	Ordinary sil. crown	1.5175	20	30	23		h^4					12.9	63.4	4
44	Soft sil. crown.....	1.5151	41	58	48		h^5	5	25	24				
45	Light Ba flint......	1.5646	15	5	16	102	h^1	3	2	2	86	10.9	25.8	4
46	Ordinary light flint	1.5800	14	7	16	104	h^2	3	2	3	81	3.3	9.4	3
47	Heavy flint	1.6190	23	2	19	80	h^1	2	2	2	71	4.5	9.1	3

nology[18] as a standard for testing the chemical durability of glass bottles. Six well-washed bottles, after having been warmed with hot distilled water, are filled to the bottom of the neck with boiling distilled water free from carbon dioxide, and are closed tightly with a copper capsule. The filled bottles are placed immediately in a suitable steam bath at atmospheric pressure and heated for five hours, after which the contents of each bottle are transferred to a tested conical flask and boiled for fifteen minutes with a known volume of standard sulfuric acid solution. The solution is then titrated, and the sulfuric acid that had been neutralized by the alkali dissolved from the bottle is calculated to milligrams of Na_2O. Four-ounce medicine bottles are not satisfactory if the Na_2O dissolved exceeds five milligrams. An account of the work preliminary to the adoption of the test was given by Turner[19]; and Cousen[20] gave a critical discussion of the method. He found that the reproducibility of the test was about 0.2 mg. Na_2O per sq. decimeter, and that the chief cause of variation was change in the rate of boiling of the water. To allow for variability in the area of bottles of the same volume, four ounces, he suggested that results be expressed as mg. Na_2O per sq. dec. of surface, on which basis the above specification becomes 3.3 mg. per sq. decimeter.

Autoclave methods, in which the samples are heated with water under pressure, have been used frequently, but they give a drastic treatment which often rates the chemical durability of various glasses in an order at variance with actual service. The severity of the attack differs according to whether the glass is exposed to liquid, to steam, or to both, and most attack is found where glass passes through the liquid-vapor surface. Turner[21] concluded that the autoclave test must be used with discretion, and in any case its findings will not necessarily apply to glass used at normal atmospheric pressure. Haigh[6] made numerous tests by the autoclave method, with the results given in Table IV. 3, and Rexer[7] also tested the method. The conclusions of these observers agreed with those of Turner.

Morey and Bowen[22] studied the action of water at temperatures of 300° and 550° C. on a number of optical glasses, and on some commercial glass tubing. They found the "soft crowns" were badly decomposed at 300° C., and completely decomposed at 550° C., in one case with the formation of a hydrous glass containing 2.6 per cent of water. As the content of lead oxide was increased in the flint glasses, the durability increased, and the extra-dense flints showed a remarkable resistance to water. The extreme conditions used in these experiments make it

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[18] Anon., *J. Soc. Glass Tech., Proc.*, **15**, 52 (1931).

[19] Turner, W. E. S., *J. Soc. Glass Tech.*, **19**, 171 (1935).

[20] Cousen, A., *J. Soc. Glass Tech.*, **20**, 418 (1936).

[21] Turner, W. E. S., *J. Soc. Glass Tech.*, **6**, 30 (1922).

[22] Morey, G. W., and Bowen, N. L., *J. Soc. Glass Tech.*, **11**, 97 (1927).

impossible to draw conclusions concerning the glasses under ordinary conditions.

The use of powders as a means of accelerating the attack on the glass has much to recommend it, and has been used by several investigators. Powder methods have been adopted as standard tests for chemical durability by the English Society of Glass Technology and by the Deutsche Glastechnische Gesellschaft; and they have been tested by a Committee of the Glass Division of the American Ceramic Society. Thomas[23] summarized the widely differing conditions, specified by several investigators, in a table, reproduced with additions as Table IV. 4. Exact adherence to the details of a prescribed experimental procedure is essential in measurements on chemical durability, because these details determine the result obtained. There is no right answer to the chemical durability of glass, no ideal number to be approximated by improvements in procedure. Rather, under each different set of experimental conditions, values are obtained which differ from those obtained under

TABLE IV. 4—Comparison of the Experimental Details of the Powder Method as Specified by Several Authors

After Thomas

Author and lit. ref.	Duration of heating (Hours)	Quantity of glass powder *a*	Grain size, (mm.)	Ratio of limiting grain sizes	Vol. H_2O, (cc.) *b*	Temp., (° C.) *c*
Mylius[1]	5	20 *g.*, *d.*2.584	0.57 to 0.73	1:1.28	70	Boiling
Keppeler[2]	5	20 *g.*, *d.*2.584	0.62 to 0.73	1:1.18	70	Boiling
Peddle[3]	1	5 *g.*	<ca.0.08	1:∞	100	80
Turner[4]	1	5 *g.*	0.5 to 0.8	1:1.6	250	Boiling
Turner[4a]	1	10 *g.*	0.5 to 0.8	1:1.6	500	Boiling
Keppeler and Ippach[5]	5	20 *g.*, *d.*2.584	0.116 to 0.190	1:1.76	100	Boiling
Fischer and Tepohl[6]	3	1 cc.	0.15 to 0.30	1:2	50	80
Enss[7]	7	18 *g.*, *d.*2.54	0.5 to 1.0	1:2	100	100
German[8]	5	10 *g.*, *d.*2.5	0.3 to 0.49	1:1.63	100	100
American No. 1[9]	4	10 *g.*, *d.*2.5	0.30 to 0.49	1:1.63	50	90

a When the density of the glass is given, the weight of sample is to be changed proportionately for glasses of different density.

b Water is used in every method except the American Tentative No. 1, which uses 50 *N* H_2SO_4.

c When the temperature is given as boiling, the temperature of a freely-boiling water-bath is meant; when given as 100° a salt bath must be used.

[1] Mylius, F., *Ber.*, **22**, 310 (1889).

[2] Draller, R., and Keppeler, G., "Die Glasfabrication," Munich and Berlin, 1926.

[3] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 36 (1920).

[4] Turner, W. E. S., *J. Soc. Glass Tech.*, **6**, 30 (1922); Dimbleby, V., and Turner, W. E. S., *J. Soc. Glass Tech.*, **10**, 304 (1926).

[4a] Private communication to Thomas.

[5] Keppeler, G., and Ippach, H., *Sprechsaal*, **60**, 239 (1927).

[6] Fischer, E., and Tepohl, W., *Glastech. Ber.*, **4**, 137 (1926).

[7] Enss, J., *Glastech. Ber.*, **5**, 449 (1928).

[8] Thomas, M., *J. Soc. Glass Tech.*, Proc. 12, 86, 104 (1928).

[9] Report of Committee on the Chemical Durability of Glass, *Bull. Am. Ceram. Soc.*, **14**, 181 (1935).

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[23] Thomas, M., *J. Soc. Glass Tech.*, *Proc.*, **12**, 86 and 104 (1928).

other conditions, and there is no *a priori* reason for accepting any one of these values or procedures as correct.

The preparation of the sample requires close attention to details of procedure, if results obtained in different laboratories are to be comparable. This was shown by the experience of the American committee,[24] which found it necessary to prescribe the use of a standard mortar. The glass must be graded between two sizes of screens, to obtain powders of comparable dimensions. The American committee found that about 11 grams was the best size of sample to be sieved at one time, and that 25 grams was an upper limit. Berger and his associates [25] made a study of the effect of various factors on the crushing and sieving of glass samples for tests of chemical durability. They concluded that: (1) the glass samples should be well-annealed, thick pieces, not of any strongly marked form; (2) crushing should not be done in too small a mortar, and the stamp should be adjusted by a stop to come within only two millimeters of the bottom of the mortar; (3) after one or at the most two crushings, the small glass should be given a preliminary sieving for 30 seconds. The residue should be crushed once or twice, then sieved, and this preliminary treatment should be continued until only a small sample remains on the screen. This preliminary sieving should be done with a screen of larger mesh than that of the larger of the two main screens, to ensure an equal volume distribution of the grains. (4) For the main sieving the previously screened material should be fed onto the main sieve, and shaken mechanically for two five-minute periods with a single clearing of the adhering grains from the sieve. (5) The sample should be washed with water-free alcohol (or better, ether) with gentle shaking. Briquetted fine dust should be removed by hand, using tweezers or a suction tube. When the above precautions are closely observed, a sample having a grain size between 0.30 mm. and 0.49 mm. will have a surface of 285 sq. cm. per cc. of solid volume of powder.

The samples are coated with a fine powder, which must be removed. The best method seems to be a gentle washing with water-free neutral alcohol. Too vigorous or too prolonged agitation with the alcohol causes continued grinding between the particles. The amount of action by the solvent may be estimated by complete analysis of the solution, as was done in some cases by Mylius and Foerster;[26] by evaporating the solution to dryness and weighing the residue; by titrating the solution with acid, thus estimating the amount of alkali which has been

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[24] Report of the Committee on the Chemical Durability of Glass of the Glass Division of the American Ceramic Society, *Bull. Am. Ceram. Soc.*, **14**, 181 (1935).

[25] Berger, E., Geffken, W., and Stoesser, K. V., *Glastech. Ber.*, **13**, 301 (1935); Berger, E., and Geffken, W., *ibid.*, **14**, 441 (1936); Berger, E., *J. Soc. Glass Tech.*, **20**, 384 (1936).

[26] Mylius, F., and Foerster, F., *Z. Instrumentenk.*, **9**, 117-22 (1889).

extracted; or by filtering and weighing the glass powder remaining undissolved. These two latter methods were compared by Peddle,[27] who found that, in the case of some inferior glasses, the amount of dissolved alkali as determined by titration was greater than the loss in weight, a result confirming the conclusion, often found in the literature, that glass tends to absorb a considerable quantity of water.

The Committee on Chemical Durability of the Glass Division of the American Ceramic Society tested a method proposed by O. G. Burch,[28] known as Tentative Method No. 1, which consists of treating a powdered sample for four hours at 90° C. with 50 cc. of $0.02N$ H_2SO_4, and determining the amount of H_2SO_4 neutralized by the Na_2O extracted from the glass by titrating the excess acid. Three or four 30- to 40-gram samples are crushed in a special hardened steel mortar, with a flat-bottomed cavity two inches in diameter, by striking the flat-bottomed pestle three or four times with a hammer. The crushed glass is then transferred to a nest of sieves of 20, 40, and 50 meshes to the inch, of which the last two give particles ranging in size from 0.295 to 0.417 mm. After shaking by hand for two minutes, the glass on the 20- and the 40-mesh sieves is again crushed and sieved, and the process repeated. The nest of sieves is shaken by machine for five minutes, or by hand for three minutes, using a rotary motion following a circle about six inches in diameter and making about 120 revolutions per minute.

The material on the 50-mesh sieve is transferred to a sheet of paper and any particles of iron are removed with a magnet; it is then put into a basket made of 80-mesh copper screen, agitated for one minute in distilled water and one minute each in two changes of alcohol, dried at 110° C., and cooled in a desiccator.

A sample of the powder weighing 10 grams, for a glass of density 2.5 or a proportional amount of a glass of different density, is then put into a 250-cc. Erlenmeyer flask of Pyrex chemical resistant glass; 50 cc. of $0.02N$ H_2SO_4 are added; the flask is closed with a one-hole stopper, and immersed to a depth of two inches in a bath at 90° C. After four hours, the flask is quickly cooled; phenolphthalein-red indicator is added; and the solution is titrated with $0.02N$ NaOH, free from CO_2, until it is in about one ml. excess, after which it is titrated with $0.02N$ H_2SO_4. The results are calculated to the percentage of Na_2O from 10 grams of glass.

The first test of the method, made by twenty-one coöperating laboratories, showed results on the same glass ranging from 0.047 to 0.111; the results of the analysts who reported "reasonable adherence" to the details of the method ranged from 0.063 to 0.075. The lowest result was reported on glass which had been kept in the open air for two weeks

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[27] Peddle, C. J., *J. Soc. Glass Tech.*, 4, 71 (1920).

[28] Burch, O. G., *Bull. Am. Ceram. Soc.*, 13, 200 (1934).

between crushing and testing; and therefore it was recommended that the testing be done the same day the sample was crushed. Several coöperators washed the glass powder with dilute (1:99) HCl, and a comparison showed that such washing lowered the result from 0.068 to 0.065. Later tests by seven coöperators are given in Table IV. 5. Blank experiments should be made to test the flasks. Pyrex chemical resistant flasks apparently "age" rapidly, as shown by the following successive tests on a new flask, reported in terms of dissolved alkali as Na_2O in mg.: 0.40, 0.22, 0.12, and 0.03.

TABLE IV. 5—Results Obtained in Second Trial of Method

Coop-erator	Bottle No. 1		Sheet Glass	Remarks
	1st Trial	2nd Trial		
3	0.066 (0.060–0.068)	0.080 (0.078–0.081)	0.027 (0.026, 0.027)	Braun disk grinder Crushed sample was large and not washed
		0.085 (0.083–0.086)	0.027 (0.027–0.027)	Crushed by impact
4	0.060 (0.060–0.060)	0.074 (0.074, 0.074)	0.027 (0.027, 0.027)	Gas-heated water-bath whose temperature varied more than ±0.5° from 90° C.
6	0.063 (0.058–0.067)	0.069 (0.068–0.070)	0.019 (0.019–0.020)	Used standard method except for bromthymol blue as indicator
11	0.067 (0.066–0.068)	0.068 (0.067–0.069)	0.019 (0.018–0.020)	Used standard method
17	0.075 (0.074–0.076)	0.076 (0.076, 0.076)	0.025 (0.025, 0.025)	2-in. mortar with rounded cavity
20	0.093	0.085 (0.081, 0.089)	0.031 (0.031, 0.031)	Mortar ⅝ in. and temperature 92.5 ±1.5° C.
21	0.111 (0.110–0.111)	0.067 (0.065–0.068)	0.020 (0.020–0.021)	1-in. mortar used in 1st trial, standard mortar in 2nd trial
16	0.072 (0.071, 0.073)		0.019 (0.019–0.020)	Used standard method

Taylor and Smith[29] and Taylor[30] compared the action of 0.02N H_2SO solution, according to the Tentative Method No. 1, with the action of water and 0.02N NaOH, at 25° and at 90°, with the results summarized by Fig. IV. 2. The compositions of the glasses used are given in Table IV. 6; the six glass compositions were all in commercial use, and appeared satisfactory as to durability under the respective service conditions to which each glass was subjected. The six variations in method placed the glasses in six different series of durability. The same six glasses also were compared by determining the rate of extraction of alkali by water at 25° for periods of from one to 72 hours, by loss in weight in treating at 90° for 100 hours, by a "dimming" test, and by weighing the residue obtained by evaporating the solution obtained by heating the glass with water in sealed test-tubes at the temperatures given in Table IV. 7. The acceleration of the rate of decomposition caused by increase in temperature and pressure differed for each glass. Glasses *B* and *D* behaved differently over the temperature range studied, the curves crossing at 140°. Glasses *A* and *E* were made into condensers and subjected to escaping steam for 100 hours, under which condition glass *E* lost 13 times as much weight as glass *A*.

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[29] Taylor, W. C., and Smith, R. D., *J. Am. Ceram Soc.*, **19**, 331 (1936).

[30] Taylor, W. C., *J. Soc. Glass Tech.*, **20**, 405 (1936).

Taylor and Smith concluded that the Tentative Method No. 1 is a convenient method of comparing the chemical durability of soda-lime-silica glasses of the types commonly used for bottles and for sheet glass, but that it may give misleading results when applied to other types of glass. "The question may fairly arise, however, as to what is general durability. Some glasses are affected more by temperature of solution, some more by alkali, others more by acid, etc. Any single method we use for comparison is therefore not completely fair to all glasses, and is a compromise . . . Durability tests on glass, as glass, must not be

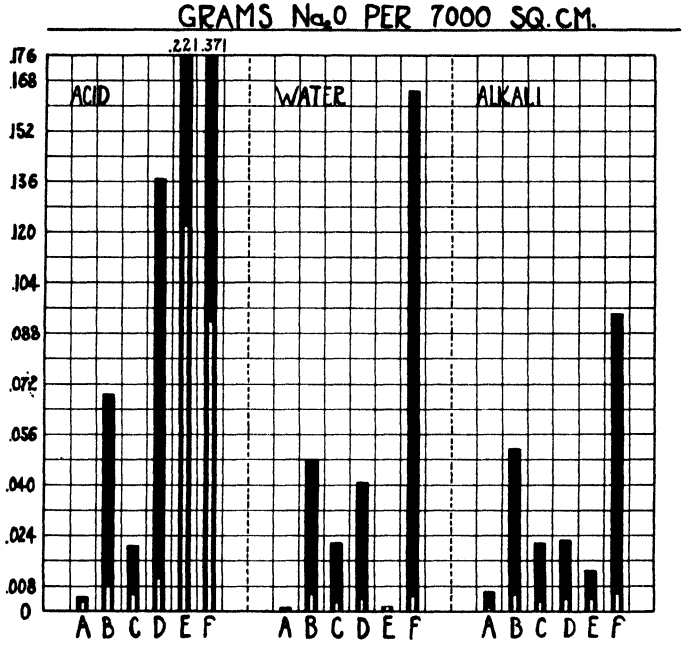

FIGURE IV. 2.—Comparison of the Action of Several Solutions on Six Different Glasses at 25° and 90° C. After Taylor and Smith.

TABLE IV. 6—Compositions of the Glasses Studied by Taylor and Smith, with Results Shown in Fig. IV. 2

Glass	SiO_2	B_2O_3	Na_2O	K_2O	MgO	CaO	PbO	R_2O_3
A	81	13	4					2
B	73		17		3	5		1
C	72		13		5	9		1
D	63		7	7			22	1
E	35		7				58	
F	60	29	8					3

confused with durability tests on glass products. Factors other than glass composition may have some influence on the durability of a product, because of the different uses to which glass is put."

Systematic Researches

Experimental Glasses. With but few exceptions, all the systematic work on the relation between composition and the power of resisting corrosion has been done in recent years. The work of Mylius and Foerster[26] was an exception, but they used only a limited series of glasses, from $2K_2O \cdot 6SiO_2$ and $2Na_2O \cdot 6SiO_2$ to $K_2O \cdot CaO \cdot 6SiO_2$ and $Na_2O \cdot CaO \cdot 6SiO_2$. Their results showed a better chemical durability for soda glasses than for potash glasses made up to the same molecular formula, and hence containing a greater percentage by weight of alkali, and also showed that the difference between soda and potash glasses decreases with increasing lime content. They found that the ratio of alkali to silica in the solution increased to a maximum at about three parts of alkali to one of lime, and then decreased, the ratio being approximately unity for alkali to lime ratios of 7:1 and 1:1.

TABLE IV. 7—Attack by Water in Glass in Sealed Tubes*

After Taylor and Smith

Glass	25° C.	65° C.	95–96° C.	20 lb.	40 lb.	60 lb.	80 lb.	100 lb.	205° C.	260° C.	265° C.
A				0.0002	0.0005	0.0017	0.0020	0.0034	0.0128	0.0301	
				.0000	.0005	.0012	.0020	.0039	.0147		
				.0005	.0005	.0015	.0020	.0027			
					.0007		.0015	.0032			
				.0002	.0005	.0015	.0019	.0033	.0138	.0301	
Av.											
B_1	None	0.0009	0.0051	.0096	.0132	.0155	.0255	.0346			
	None	.0009	.0047	.0089	.0125	.0189	.0252	.0337			
Av.	None	.0009	.0049	.0093	.0129	.0172	.0254	.0342			
D		.0006	.0013	.0024	.0106	.0305	.0535	.0928			
		.0005	.0013	.0026	.0127	.0225	.0582	.1013			
Av.		.00055	.0013	.0025	.0117	.0265	.0554	.0971			
E						.00050		.0010			.0138
						.00025		.0012			
Av.						.0004		.0011			.0138

* Area exposed approximately 40 square centimeters; residue in grams calculated to 100 square centimeters as weighed in a platinum dish after 6 hours at temperature and pressure.

The most extensive body of data on the resistance of glass to water with reference to chemical composition is that of Peddle, representing development work carried out during the World War. The samples of glass were powdered to pass a 160-mesh sieve and five grams of the powder were digested with distilled water for one hour at 80°. The amount of undissolved material was determined by filtration; the amount of acid required to neutralize the filtrate was obtained by titration; and the data were recalculated to a 100-gram sample.

Measurements were made on all the types of glass studied by Peddle, of compositions given in Table XVI. 9. Table IV. 8 contains the soda-lime-silica glasses, and in addition it shows the effect of exposing polished specimens to moist air at 18° for 100 hours, and to ordinary atmospheric conditions for one year. Data are given for three series of glasses: *163,* obtained by adding increasing amounts of CaO to the sodium silicate glass 100 $SiO_2 + 40 Na_2O$; *165,* similarly obtained from $100 SiO_2 + 20 Na_2O$; and *171,* obtained by altering the ratio of CaO to Na_2O, keeping SiO_2 constant. The results of the *171* series were not entirely consistent with those of the others.

TABLE IV. 8—Chemical Durability of Soda-Lime-Silica Glasses

After Peddle

No.	Action of water at 80° on 100 grams of glass powder		Exposure Tests	
	Grams dissolved	Grams alkali by filtration	100 hours to moist air at 18°	One year to ordinary atmospheric conditions
		Series $100SiO_2 \cdot 40Na_2O \cdot xCaO$		
163 A	24.854	11.670	Greasy film; drops of liquid	Glass dull; covered with white crystalline powder
B	6.724	5.664	Slight greasy film	Glass dull; signs of crystals
C	2.504	2.694	Very slight greasy film	Glass dull; signs of crystals
D	1.676	2.361	Signs of being affected	Glass dull; surface spotted
E	1.296	1.444	Unaltered	Glass dull; surface spotted
F	0.474	0.672	Unaltered	Surface dull in patches
		Series $100SiO_2 \cdot 20Na_2O \cdot xCaO$		
165 A	2.662	1.915	Unaltered	Surface dull in patches
B	1.214	0.845	Unaltered	Slight signs of filming
C	1.186	0.419	Unaltered	Unaltered
D	0.670	0.253	Unaltered	Unaltered
E	0.530	0.217	Unaltered	Unaltered
F	0.272	0.157	Unaltered	Unaltered
		Series with weight per cent SiO_2 *constant*		
171 A	1.840	3.364	Covered with wet spots	Very pronounced film all over surface
B	0.952	1.036	Very greasy	Pronounced film all over glass
C	0.688	0.276	Slightly greasy	Filmed all over
D	0.420	0.185	No effect	Extremely slight film
K	1.196	0.710	Slightly greasy	Faint film
M	1.214	0.360	Slightly greasy	Faint film
N	0.864	1.255	Slightly spotted	Faint film
L	0.772	0.530	Slightly greasy	Faint film

A comparison of similar compositions containing CaO, BaO or PbO as the variant oxide, gave evidence of the superiority of the CaO glasses. Highly resistant glasses containing BaO and PbO can be obtained only by adding greater percentages of these oxides than would be possible without devitrification in the CaO glasses. With the exception of glasses containing only a small amount of alkali, the glasses containing BaO gave better chemical durability than those containing PbO.

Besides the above glasses in which Na_2O was the only alkali, Peddle prepared glasses in which K_2O was the only alkali, and glasses containing both alkalies in variable proportions; and each of these was studied by the separate addition of CaO, BaO and PbO to the alkali silicate. The potash glasses containing CaO were of greater chemical durability than those containing BaO or PbO, and the glasses containing BaO were better than those containing PbO, except when the alkali content was small. These conclusions were true also for the soda glasses. The potash glasses were usually of greater chemical durability than the soda glasses, when comparison was made of glasses containing the same percentage by weight of alkali oxide, although the differences were not large. Glasses containing both alkalies were better than those contain-

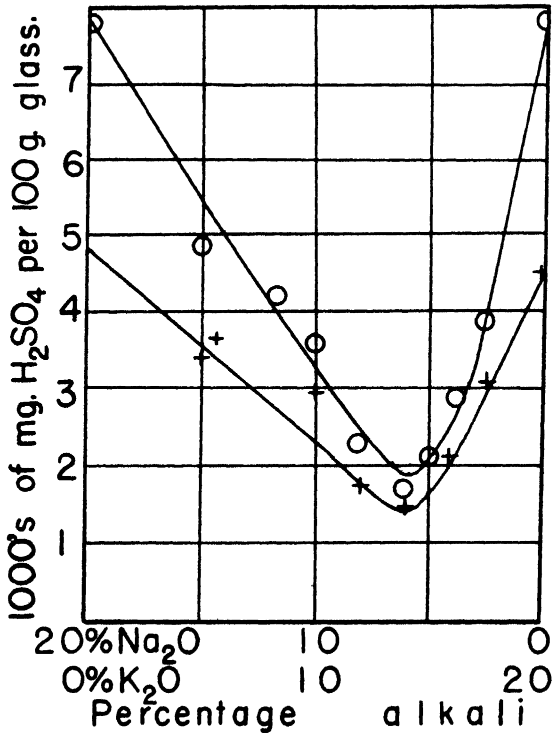

FIGURE IV. 3.—Chemical Durability of Glasses of the Formulas 20% (Na_2O + K_2O) + 20% PbO + 60% SiO_2 (Upper Curve) and 20% (Na_2O + K_2O) + 30% PbO + 50% SiO_2 (Lower Curve). After Peddle.

ing either Na_2O or K_2O alone. This superiority was especially evident in the glasses containing PbO, the flint glasses, concerning which he concluded:[31] "A mixture of equal percentages of soda and potash has a remarkable effect upon solubility. Below a total alkali content of 20 per cent, a glass containing equal percentages of both soda and potash has a much lower solubility than a glass containing the same amount of alkali in the form of soda or potash alone." Hodkin and Turner[32] came to the same conclusion. In a later publication Peddle[33] gave the results obtained from a study of glasses in which the percentage of SiO_2 and PbO was kept constant, and the ratio of Na_2O to K_2O varied. Four series of such glasses were studied, whose percentage compositions by weight were: 20% ($Na_2O + K_2O$) · 20% PbO · 60% SiO_2; 20% ($Na_2O + K_2O$) · 30% PbO · 50% SiO_2; 10% ($Na_2O + K_2O$) · 30% PbO · 60% SiO_2; and 10% ($Na_2O + K_2O$) · 40% PbO · 50% SiO_2. The results were summarized by means of two curves, reproduced as Fig. IV. 3; the measure of the attack by water in these curves was the number of milligrams of H_2SO_4 required to neutralize the alkali dissolved from 100 grams of glass when treated as previously described. Peddle concluded: "To obtain maximum durability in an alkali-lead-silicate glass, the best proportion in which to mix the alkalies is in the ratio of 7 parts of potash to 3 parts of soda. This ratio holds good for all percentages of alkali below 20, and is independent of the amount of SiO_2 or PbO in the glass."

Turner and his collaborators[34] carried out systematic experiments with soda-lime glasses, in which CaO, MgO, Al_2O_3, B_2O_3, or TiO_2 replaced part of the Na_2O in the glass $Na_2O \cdot 3SiO_2$. The compositions of the glasses are given in Table X. 3. Two types of testing methods were used, in one of which 10 grams of powdered glass, sieved between 20- and 30-mesh, and contained in a bag of 90-mesh platinum gauze, were boiled in water for one hour, and the loss in weight and the amount of alkali set free were determined. The results given in Table IV. 9 show that the lime glasses are the poorest, with the titania and magnesia glasses in the order named, but differing little from each other.

The soda-lime and soda-magnesia glasses of the preceding series were subjected to other tests, the results of which are reproduced for comparative purposes. Discs of the various glasses, approximately 6.5 cm. in diameter, were suspended in a carrier of silver wire, completely immersed in the test solution, which was contained in a chemically resistant beaker of silica glass, resistant glass, or silver, and the solutions were kept approximately constant in composition by the condensing

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[31] Peddle, C. J., *J. Soc. Glass Tech.*, **4,** 120 (1920).

[32] Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **4,** 120 (1920).

[33] Peddle, C. J., *J. Soc. Glass Tech.*, **5,** 195 (1921).

[34] Cauwood, J. D., Clarke, J. R., Muirhead, C. M. M., and Turner, W. E. S., *J. Soc. Glass Tech.*, **3,** 228 (1919). Dimbleby, V., Muirhead, C. M. M., and Turner, W. E. S., *ibid.*, **6,** 101 (1922). Dimbleby, V., English, S., Hodkin, F. W., and Turner, W. E. S., *ibid.*, **8,** 173 (1924). Sheen, A. R., and Turner, W. E. S., *ibid.*, **8,** 187 (1924). Dimbleby, V., and Turner, W. E. S., *ibid.*, **10,** 304 (1926).

TABLE IV. 9—Action of Boiling Water and Boiling Solutions on Glasses of the Formula xRO (or R_2O_3 or RO_2) $(2-x)$ Na_2O $6SiO_2$

After Dimbleby and Turner

Percentage Loss in Weight and Na_2O Extracted

Mols. Oxide per 100 mols. SiO_2	CaO		BaO		PbO		MgO		ZnO		Al_2O_3		ZrO_2		TiO_2	
	Loss	Na_2O	Loss	Na_2O	Loss	Na_2O	Loss	Na_2O	Loss	Na_2O	Loss	Na_2O	Loss	Na_2O	Loss	Na_2O
2	23.0	8.20	43.70	17.60	17.0	6.7	...	...	10.80	7.18	...	...	2.60	1.80	7.55	1.54
4	2.42	2.35	13.0	5.50	2.0	1.75	2.25	1.39	1.26	1.57	0.68	0.59	0.58	0.38	1.28	0.27
6	0.90	1.00	2.96	1.90	0.7	0.60	0.88	0.76	0.40	0.30	0.35	0.24	0.22	0.19	0.55	0.13
8	0.45	0.50	0.8	0.68	0.35	0.25	0.42	0.29	0.20	0.18	0.20	0.09	...	...	0.28	0.07
10	0.34	0.25	0.4	0.22	0.29	0.10	0.25	0.13	0.16	0.12	0.17	0.03	...	...	0.12	0.05
12	0.25	0.10	0.38	0.12	0.22	0.10	0.15	0.07	0.12	0.06	...	...	...	...	0.10	0.03
14	0.21	0.05	0.34	0.06	...	...	0.12	0.05	0.10	0.04	...	...	...	...	0.09	0.02
16	0.17	0.04	0.24	0.04	...	...	0.10	0.03	0.10	0.02	...	...	...	...	0.08	0.01
18	0.17	0.02	...	...	...	...	0.06	0.02	...	...	...	...	...	...	0.08	0.01
20	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.08	0.008

Percentage Loss in Weight on Boiling for 1 Hour in

20.24% HCl, 2*N*-Na_2CO_3, and 2*N*-NaOH, Powdered Glasses of Grains 20-30 Mesh

General Composition of Glasses: $6SiO_2$ $(2-x)$ Na_2O, xRO (*or* R_2O_3 *or* RO_2)

Mols. RO etc., per 100 mols. SiO_2	HCl								Na_2CO_3								NaOH							
	CaO	BaO	PbO	MgO	ZnO	Al_2O_3	ZrO_2	TiO_2	CaO	BaO	PbO	MgO	ZnO	Al_2O_3	ZrO_2	TiO_2	CaO	BaO	PbO	MgO	ZnO	Al_2O_3	ZrO_2	TiO_2
2	...	4.5	2.5	...	1.8	...	1.8	2.0	...	38.0	23.4	...	11.2	...	2.0	11.3	...	5.6	3.06	...	3.7	...	1.3	...
4	1.25	2.0	1.0	1.4	0.85	0.9	0.6	1.0	6.8	7.0	3.2	...	2.5	1.0	0.9	2.4	2.6	3.8	3.10	3.1	3.2	2.8	0.8	6.0
6	0.43	1.0	0.5	0.7	0.5	0.4	0.4	0.5	2.8	4.9	2.2	4.1	0.5	0.6	0.6	1.6	2.3	3.0	3.18	2.8	2.8	2.5	0.7	...
8	0.26	0.5	0.4	0.4	0.3	0.2	...	0.3	2.4	4.0	2.12	3.2	0.4	0.4	...	1.1	2.1	2.5	3.20	2.5	2.4	2.5	...	...
10	0.19	0.3	0.4	0.3	0.2	0.2	...	0.2	2.0	3.5	2.08	2.5	0.3	0.4	...	0.9	2.0	2.3	3.25	2.7	2.2	2.6	...	3.6
12	0.16	0.24	0.3	0.2	0.16	...	...	0.2	1.9	3.2	2.0	2.1	0.2	...	...	0.8	1.7	2.2	3.26	2.1	2.1	...	...	3.2
14	0.13	0.22	...	0.2	0.1	...	...	0.2	1.5	2.6	...	2.0	0.2	...	...	0.7	1.5	1.9	...	2.1	1.9	...	...	2.9
16	0.11	0.20	...	0.1	0.1	...	...	0.1	1.3	2.2	...	1.9	0.2	...	...	0.7	1.2	1.7	...	2.1	1.7	...	...	2.6
18	...	...	...	...	...	...	...	0.1	...	...	...	...	...	...	...	0.6	...	...	...	...	...	...	...	2.4
20	...	...	...	...	...	...	...	0.1	...	...	...	...	...	...	...	0.5	...	...	...	...	...	...	...	2.3

action of a basin of cold water covering the beaker. The reagents employed were water, $2N$ NaOH, $2N$ Na_2CO_3, and 20.24 per cent (constant boiling) HCl. The results are assembled in Table IV. 9.

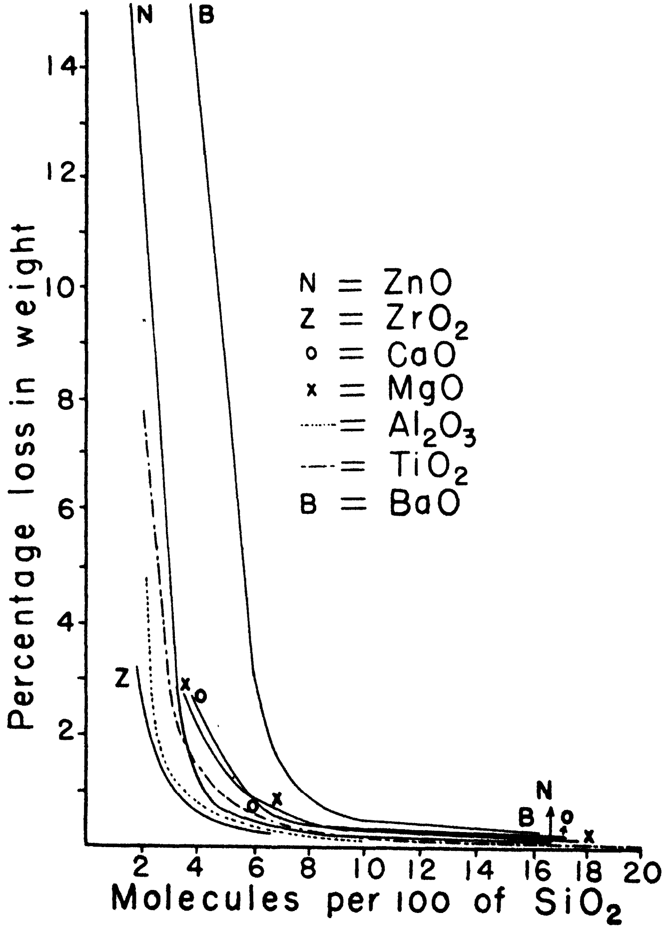

FIGURE IV. 4.—Percentage Loss in Weight of Powdered Glasses on Treatment with Boiling Water. After Dimbleby and Turner.

Comparison of the soda-lime and soda-magnesia trisilicate glasses showed that the "magnesia glasses appear to possess a slight advantage over lime glasses in regard to corrosion by water; to show no advantage in the case of hydrochloric acid; and to be decidedly inferior when the corrosive agent is an alkaline solution."

A further series of experiments[35] was made on the soda-lime glasses,

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[35] Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **6**, 291-308 (1922).

in which the discs were heated with water in an autoclave to various temperatures and corresponding pressures. The original article gave a number of photographs illustrating the appearance of the discs after treatment, as well as tables showing the loss in weight in water and in steam, and also the amount of alkali extracted by water. The results were irregular; in many cases the loss in weight was less than the Na_2O extracted, which showed that the glass had taken up water, and in other cases the specimen exposed to steam showed as much, or even more loss in weight than that in water. Hodkin and Turner did not recommend the autoclave as a universal test for the durability of glassware.

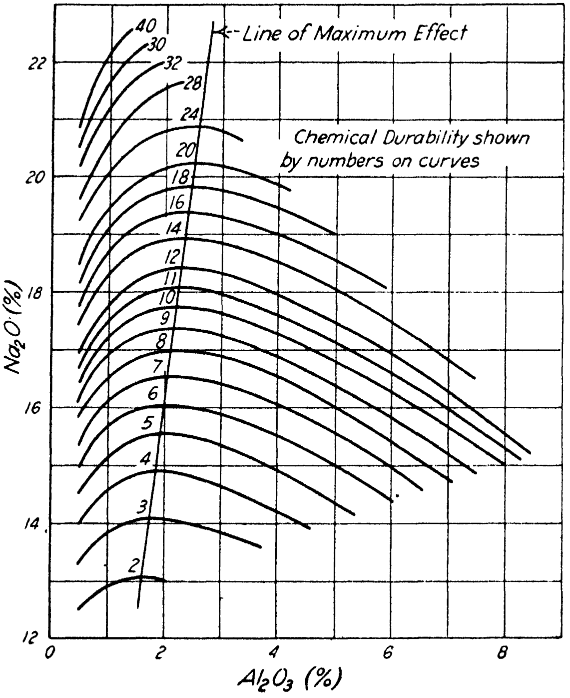

Figure IV. 5.—The Chemical Durability of Soda-Lime-Silica Glasses as Affected by the Addition of Alumina, showing the Line of Maximum Effect. After Lyle, Horak and Sharp.

Fig. IV. 4 shows the effect on chemical durability of replacing sodium oxide by other oxides in trisilicate glasses, according to experiments by Turner and his associates. They found that zirconia, closely followed by alumina and titania, was most effective in increasing chemical durability. Zinc oxide and magnesia were the most effective of the "basic" oxides in increasing durability, and calcium oxide, lead oxide and barium

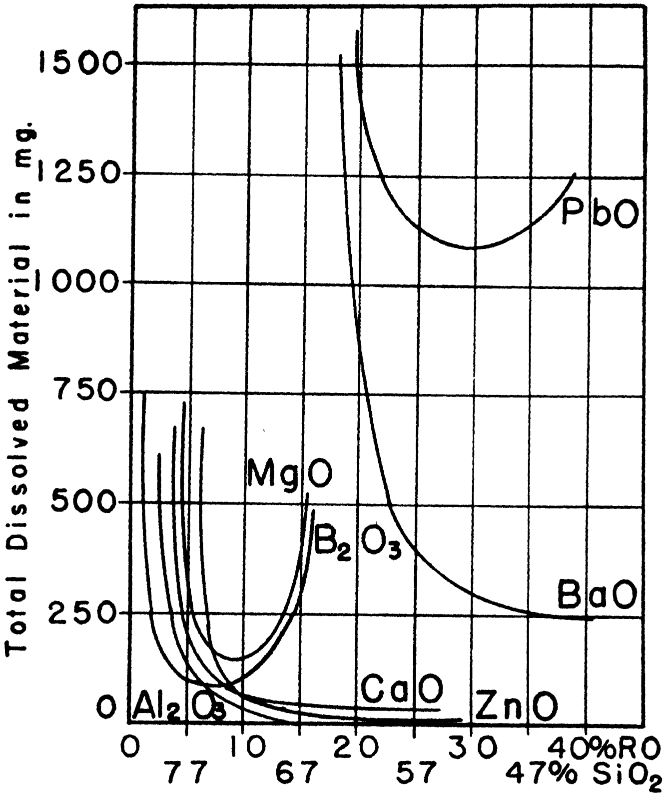

FIGURE IV. 6.—Chemical Durability of Glasses of the Formula, in Percentage by Weight, $18Na_2O + 82\ (SiO_2 + RO \text{ or } R_2O_3)$. After Enss.

oxide gave glasses of durability decreasing in the order mentioned. Chemical durability also was improved when silica was replaced by zirconia, for the zirconia glasses showed excellent resistance to water, hydrochloric acid, sodium carbonate and sodium hydroxide.

The value of alumina in increasing chemical durability has long been known. Lyle, Horak, and Sharp[36] made a study of the effect of alumina, using a powder method in which water was the attacking agent. The results obtained with glasses containing Na_2O, CaO, Al_2O_3, and SiO_2 were represented by the formula:

$$\log D = -6.427 + 5.89 \log (N + A) - 0.654 \log A,$$

in which D represents the durability in terms of the number of cc. of $0.02N\ H_2SO_4$ required to neutralize the alkali extracted from 10 grams

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[36] Lyle, A. K., Horak, W., and Sharp, D. E., *J. Am. Ceram. Soc.*, **19**, 142 (1936).

of glass, and *N* and *A* represent the percentages of Na_2O and Al_2O_3. The results are shown in Fig. IV. 5, in which the locus of maximum effect is indicated.

Enss[37] used a powder method, details of which are in Table IV. 4. In each of a series of glasses obtained from a parent glass having the percentage composition by weight: SiO_2, 82, Na_2O, 18, step-wise replacement of SiO_2 by each of the oxides Al_2O_3, ZnO, CaO, B_2O_3, MgO, BaO, and PbO increased the chemical durability, as indicated in Fig. IV. 5. In this figure are given the total weights in milligrams of dissolved material; these were obtained by evaporation of the extracting liquid and analysis of the residue. In the more durable glasses the amount of SiO_2 in solution was less than the amount of Na_2O, but in the less durable glasses the SiO_2 was in excess. The order in which the oxides are given above is that of the chemical durabilities when 10 per cent of the oxide had been added; for example, of a glass of percentage composition SiO_2, 72, Na_2O, 18, (MO or M_2O_3), 10, the alumina glasses of this composition are best, the PbO glasses worst. The pronounced minimum found with B_2O_3 and MgO is noteworthy. The optimum ratio of Na_2O and K_2O found by Peddle was confirmed, but Enss found a smaller effect.

TABLE IV. 10A—Action of Several Reagents on Glasses of Composition Given in Table IV. 10B

After Foerster

No.	Alkali extracted by water expressed in thousandths of a milligram Na_2O		Proportion of alkali extracted by hot and cold water respectively	Weight in milligrams given up to 2*N*-alkali solution in 3 hours, at 100°		Four-hour treatment with water at 190°			Molecular ratio of silica to alkali, taken up by water at 190°
	in 8 days at 20°	in 3 hours at 80°		NaOH	Na_2CO_3	Total	Alkalies	Quantity of Na_2O corresponding to dissolved alkalies	
1	2.5	2.7	1.1	67.3	23.5	23.7	3.5	3.5	6.0
2	2.1	6.3	3.0	39.7	17.6	...	...	...	...
3	10.7	28.4	2.65	35.4	...	...	...	...	...
4	8.9	28.2	3.17	37.5	59.5	17.2	5.6	4.6	2.65
5	13.1	26.8	2.05	...	...	...	...	...	...
6	14.0	56.0	4.0	39.8	76.9	...	...	...	...
7	14.5	45.0	3.10	37.7	79.2	51.3	15.4	11.1	3.35
8	14.9	50.0	3.40	38.5	73.0	...	...	...	...
9	17.8	66.0	3.72	42.4	79.4	67.0	16.4	14.7	3.57
10	16.6	65.0	3.91	46.5	23.0	34.0	6.4	6.4	4.42
11	27.0	98.0	3.63	31.3	40.7	?	7.3	7.3	...
12	...	...	...	...	...	63.0	16.2	10.7	4.5
13	...	...	...	...	...	37.0	8.3	8.3	3.6
15	32.0	217.0	6.78	...	...	...	...	...	...
16	77.0	654.0	8.5	46.0	45.0	126.0	61.0	52.0	1.3
17	74.0	356.0	4.73	58.0	51.0	...	...	...	...

Commercial Glasses. A large number of studies have been made of the resistance of commercial glasses to attack by reagents; but because

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[37] Enss, J., *Glastech. Ber.*, 5, 1 (1928).

they were made by different observers and by different methods, the conclusions are rarely comparable. On the following pages are reproduced the results of some of the most extensive studies, especially those in which the glasses were analyzed and commercial types were identified by name.

The first selections are from the work of Foerster,[38] who studied the action of water and of aqueous solutions on a variety of glass types. Table IV. 10A summarizes the tests, and the compositions of the glasses are given in Table IV. 10B; Nos. 1, 2, and 10 are Jena 59^{III} (borosilicate thermometer glass), 165^{III}, and 16^{III} (normal thermometer glass).

TABLE IV. 10B—Compositions of the Glasses of Table IV. 10A

No.	SiO_2	B_2O_3	K_2O	Na_2O	CaO	ZnO	MnO	Al_2O_3 and Fe_2O_3
1	71.95	12.0	. . .	11.0	. . .	. . .	0.05	5.0
2	74.4	. . .	. . .	9.8	7.0	5.0	0.3	3.5
3	75.9	. . .	5.8	7.6	10.4	. . .	. . .	0.3
4	76.6	. . .	6.6	6.7	9.5	. . .	. . .	0.6
5	76.8	. . .	6.2	6.4	10.0	. . .	0.2	0.4
6	76.3	. . .	7.0	8.3	8.1	. . .	. . .	0.3
7	75.1	. . .	11.8	4.9	7.6	. . .	0.1	0.5
8	77.6	. . .	4.3	10.0	7.8	. . .	. . .	0.3
9	77.2	. . .	4.6	10.1	7.7	. . .	. . .	0.4
10	67.5	2.0	. . .	14.0	7.0	7.0	. . .	2.5
11	70.6	. . .	0.6	14.3	11.2	. . .	0.4	2.9
12	78.9	. . .	14.0	1.0	5.8	. . .	0.1	0.2
13	73.0	. . .	1.8	12.9	11.0	. . .	. . .	1.3
15	74.1	. . .	9.7	9.0	6.8	. . .	trace	0.4
16	68.9	. . .	6.7	13.7	7.2	. . .	0.3	3.2
17	57.3	. . .	12.7	. . .	. . .	PbO 30.0	. . .	. . .

Foerster concluded, on the basis of these and of subsequent tests, that the resistance of glass to water was primarily dependent on the alkali, and that there was no indication of maximum resistance at the so-called "normal" composition, $R_2O \cdot RO \cdot 6SiO_2$. Although increase in temperature decreased the resistance to attack, the effect was less marked in glasses of high CaO content than in glasses of equal initial resistance of higher SiO_2 content. The tests with water at 190° arranged the glasses in a different order from that at 20°, or even at 80°. With good glasses, it was immaterial whether K_2O or Na_2O was present in greater proportion. There was a rough parallelism between the action of water and of caustic alkali, but the glasses containing B_2O_3 were attacked more than would be expected from the results with water. Very dilute alkali, about 0.001 *N* solutions, attacked glass no more rapidly than did water, but with increase in alkali the attack increased until about 2*N* strength was reached, after which the effect remained approximately

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[38] Foerster, F., *Z. anal. Chem.*, **33**, 299 and 381 (1894). The tables are reproduced from Cauwood, J. D., English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **1**, 153 (1917).

constant until the solutions became very strong, when the attack diminished. Glasses as a rule did not differ nearly so much in susceptibility to attack by alkaline solutions as by water; and the order of alkalies with respect to decreasing amount of attack on glass was NaOH, KOH, NH_4OH and $Ba(OH)_2$. A small amount of alumina, however, had a decidedly beneficial effect. With alkali carbonate solutions the results showed still more divergence from those with water; and salt solutions as a whole showed no regularity.

Study of the effect of acids led Foerster to the conclusion that they had no direct effect, but merely diminished the proportion of water, and hence diminished the amount of attack. The first action of water was to extract alkali, which accelerated the corrosion; acid neutralized the alkali set free, and hence diminished the attack. However, glasses having low silica-content were decomposed much more rapidly by acid than by water, and the ordinary behavior of glass toward acid solutions was due to its large content of silica.

TABLE IV. 11A—Rate of Attack by Different Methods on Some Commercial Glasses

After Cauwood, English, and Turner

	Evaporation of water			Autoclave 183°					
Glass	Exposed area (cm²)	mgm. Na_2O extracted	Total loss in weight (mgm.)		mgm. Na_2O extracted	2-*N* NaOH	0.1-*N* NaOH	2-*N* Na_2CO_3	20-24% HCl
						Loss in weight (mgm. per sq. dcm.)			
A	133	0.25	0.8	39.8	0.11	387.6	64.4	92.2	31.8
B	136	0.35	1.2	34.8	2.29	276.5	60.0	90.3	15.1
C	139	0.31	0.8	38.6	4.65	292.4	62.1	83.2	9.7
D	133	0.20	1.4	41.0	2.8	239.5	53.9	74.1	7.2
E	133	0.26	0.6	32.4	2.98	283.8	61.8	78.0	8.3
F	136	0.28	0.9	29.2	nil	312.5	52.4	83.4	33.4
G	126	0.35	0.7	35.0	nil	235.8	46.0	108.1	5.1
H	135	4.23	14.4	3470.0	125.2	470.3	136.8	600.7	8.0
I	138	0.70	2.8	1435.0	26.5	343.4	90.6	203.3	5.8
J	160	1.28	6.2	1924.4	62.0	364.0	111.3	364.3	5.4
K	103	1.85	5.5	....	...	290.0	...	...	...
L	112.5	0.43	0.9	60.6	7.6	287.1	53.0	87.7	3.1
M	112	0.49	1.2	204.8	20.4	294.0	64.2	145.4	3.0
N	115	0.46	1.1	75.5	9.9	280.9	56.3	108.1	3.2
O	117	0.31	0.8	15.4	1.3	355.2	92.2	153.3	1.5
P	115	0.62	1.2	85.9	12.7	237.3	65.4	78.0	2.8
Q	141	0.37	1.4	78.6	7.9	242.9	41.0	75.9	4.3
R	139	0.95	3.7	994.6	68.7	289.1	84.4	422.5	2.0
S	139	0.04	0.5	4917.3	158.7	273.6	98.3	397.0	0.7
T	132	0.56	1.4	124.8	1.9	239.3	46.5	96.8	3.4
V	135	0.16	1.3	69.0	8.7	249.0	57.0	89.2	1.6

Turner and his co-workers made tests on a large number of analyzed commercial glasses intended for use in chemical ware. In the first [39] of these papers the previous work on the subject was reviewed, and the results of tests on a number of British glasses were compared with similar tests on new Jena glassware. These were the most elaborate

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[39] Cauwood, J. D., English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, 1, 153 (1917).

tests; foreign glasses examined subsequently were tested by the six methods which experience showed to be the most useful. (Table IV. 11A). In one method a sample was subjected to the action of water boiling on a hot plate at such a rate that 200 cc. were evaporated in two hours. The results are expressed as the loss in weight and as the amount of alkali extracted; the area exposed to the mean volume is recorded (Cols. 3, 4, 5, Table IV. 11A). In a second method a sample was subjected to the action of water and steam in an autoclave at 183°. The results are expressed as the loss in weight and as the amount (in mg.) of Na_2O extracted; the area exposed to the water was the same (155 sq. cm.) in all cases (Cols. 6, 7, Table IV. 11A). In each of the other four methods a sample was treated with a boiling solution for three equal periods of time; in the case of the three alkaline solutions (0.1 *N* NaOH, 2 *N* NaOH, and 2 *N* Na_2CO_3) each period was one hour, and in the case of the acid solution (constant boiling HCl) each was one-half hour. The results are given as the total loss of weight in milligrams per sq. dec. for the total period; in the original the results for each period were given, but little can be learned from the separate values. Table IV. 11A summarizes the result for these six tests on all glasses studied, and Table IV. 11B gives their compositions and trade names.

TABLE IV. 11B—Compositions of the Glasses of Table IV. 11A *

	Glass	SiO_2	B_2O_3	Na_2O	K_2O	CaO	ZnO	MgO	Al_2O_3	Fe_2O_3	As_2O_5	MnO
A	Jena Geräte	64.58	10.03	7.38	tr.	0.08	11.78	0.12	6.28	0.10	...	tr.
B		64.39	1.93	13.42	4.02	7.38	nil	0.10	9.07		...	...
C		65.45	7.13	11.81	0.34	0.40	9.06	tr.	6.18	0.09	...	nil
D		66.51	4.57	11.52	2.58	4.35	3.62	0.33	6.74	0.08	...	0.10
E		66.38	6.92	10.02	1.09	0.49	8.66	0.12	6.60	0.12	...	tr.
F		64.35	7.60	9.90	1.59	6.58	nil	0.22	9.84	0.10	...	tr.
G		69.40	4.01	6.46	5.92	5.78	7.35	tr.	1.00	0.12	...	0.08
H		72.03	nil	17.62	0.73	7.93	nil	0.52	0.90	0.10	...	tr.
I		71.82	2.08	15.08	1.47	5.20	3.07	0.16	1.12	0.16	...	tr.
J		73.67	1.73	13.06	3.50	7.50	nil	tr.	0.36	0.14	...	0.10
L	Nonsol	68.03	5.81	11.18	0.30	0.80	7.39	3.41	2.62	0.20	[1]	tr.
M	Insolo	69.84	4.02	11.25	0.70	1.69	3.80	6.25	0.96	0.34	[2]	tr.
N	Fry	68.58	8.0	10.01	1.29	2.65	3.60	2.53	2.90	0.20	0.18	tr.
S	German-unmarked	76.10	nil	11.16	5.60	6.30	nil	0.29	0.20	0.14	nil	0.10
T	Insol	67.42	2.35	9.92	3.06	3.14	8.12	4.50	0.65	0.21	[3]	tr.
V	Macbeth-Evans	71.03	7.44	10.74	0.30	0.64	5.30	2.61	1.57	0.35	0.05 [4]	tr.

(*1*) Sb_2O_3—0.25.
(*2*) Sb_2O_3—1.00.
(*3*) Sb_2O_3—0.65.
(*4*) Sb_2O_3—0.45.

* See Table III. 3 for composition of Glasses K, O, P, Q, R, U.

The conclusions reached from those tests were substantially in accord with the conclusions of Foerster, and with those of Walker,[40] although the testing methods used in the three sets of observations were not strictly comparable. In resistance to attack by boiling water, glasses having a high content of SiO_2, especially those containing some B_2O_3, were superior, whereas high alkali content produced an inferior glass.

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[40] Walker, P. H., *J. Am. Chem. Soc.*, **27**, 865 (1905). Walker, P. H., and Smither, F. W., *J. Ind. Eng. Chem.*, **9**, 1090 (1917).

In the autoclave tests certain glasses containing B_2O_3 proved decidedly inferior. Thus although the new Jena glass and Pyrex chemical resistant glass were best at 100° (with the exception of glass *S*, which gave inexplicably low losses at 100°), in the autoclave tests the Jena glass was inferior to many others, and Pyrex chemical resistant glass remained the best. Continued treatment with water[41] tended to improve the surface of glass, rendering it less readily attacked by water. The action of acid closely paralleled that of water; the high silica glasses were superior, with Pyrex again at the top, and the zinc-containing borosilicates slightly inferior. The action of alkalies did not parallel that of water; here the borosilicates tended to rank below the high-lime glasses. Continued treatment with alkali failed to improve the surface of glass, although continued treatment with acid usually resulted in a more resistant surface, as was the case with water.

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[41] Cauwood, J. D., and Turner, W. E. S., *J. Soc. Glass Tech.*, 2, 235 (1918).

Chapter V

The Viscosity of Glass

The viscosity of glass is of practical importance in all stages of the manufacturing process. The rate of melting glass is chiefly determined by the rate of removal of bubbles, which, in turn, is largely dependent on the viscosity; and for the proper working of glass the viscosity must be within narrow limits. This factor has become of increasing importance with the development of automatic machinery, which requires a supply of glass having not only constant viscosity but also a definite viscosity-temperature relationship determined by the type of ware and the rate of working. Besides the melting and working temperatures, the various empirical points which are used or have been proposed for characterizing glasses at lower temperatures, such as the cohesion temperature,[1] and the softening temperature, and the various definitions of the annealing temperature, are all attempts to prescribe a definite viscosity in terms capable of convenient experimental determination. Accurate knowledge of the relation between composition and viscosity and between temperature and viscosity is a matter of importance to glass manufacturers. Much has been learned in the past few years.

Definitions and Units

When a shearing force is applied to a liquid, a displacement results, and with continued application of the force a flow takes place. The ratio between the force and the displacement is a measure of the viscosity. For true viscosity the relation between flow and shear is a constant, and can be represented by a straight line passing through the origin. If the application of a small limiting shear is necessary before deformation begins, it is considered that the flow is not truly viscous, but plastic.

When the viscosity is very high, as, for example, below the annealing temperature, the viscous movements are complicated functions of the past mechanical and thermal history of the glass. The application of too great a rate of shear at low viscosities results in turbulent flow and the breakdown of the linear relation. Maxwell's definition of the coefficient of viscosity of a fluid is: "The viscosity of a substance is measured by the tangential force on unit area of either of two horizontal planes of indefinite extent at unit distance apart, one of which is fixed

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[1] These empirical points are discussed on p. 169.

while the other moves with unit velocity, the space between being filled with a viscous substance." The coefficient of viscosity is usually denoted by the symbol η and Maxwell's definition may be represented by the formula $\eta = \frac{Fs}{v}$ in which F is the force, s the distance apart of the parallel planes, and v the relative velocity of the two planes. Viscosity has the dimensions $(ML^{-1}\,T^{-1})$, and it is measured in dynes per centimeter per second, the unit of viscosity being termed a poise. The kinematic viscosity is the viscosity in poises divided by the density. Fluidity is the reciprocal of viscosity.

Methods of Measurement of Viscosity

The methods of viscosity measurement applicable to glass are limited by the experimental difficulties resulting from the high temperature and the corrosive character of the glass, and so great is the range of viscosities that different methods must be used in the various portions of the viscosity-temperature curve.

The Stokes method, in which is measured the rate of fall of a heavy body, usually a platinum ball, through the molten glass, is applicable over only a small range of low viscosity. It is subject to numerous experimental difficulties, and the corrections for deviation from the theoretical conditions are uncertain. Some of the early measurements[2] of the viscosity of glass, now of only historical interest, were made by this method.

Trouton and Andrews,[3] in studying the viscosity of pitch, determined the position of the metal ball by x-ray photographs taken at definite intervals of time. Masson, Gilbert, and Buckley[4] suggested the use of the method with glass, and Wood[5] devised an apparatus with which he measured some viscosities. Hunter[6] described a modification of the falling ball method, also described by Cohn,[7] in which the time of passage between two radio coils wound on the tube enclosing the crucible was determined by picking up the signal with a short wave receiver, and recording it on an oscillograph. The apparatus was used with four complex glasses in the approximate viscosity range from 400 to 4×10^4 poises. Cohn[8] described a simplified method, in which successive balls are dropped into the glass at appropriate intervals, the melt is cooled, and the position of the balls measured. Bacon[9] made a

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[2] Arndt, K., Z. *Chem. Apparat.*, **3**, 549 (1908); Greiner, E., *Diss.*, Jena (1907); Doelter, C., *Chem. Ztg.*, **36**, 569 (1912); Staley, H. F., *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **5**, 127 (1912).

[3] Trouton, F. T., and Andrews, E. S., *Phil. Mag.*, **7**, 347 (1904); *Proc. Phys. Soc. (London)*, **19**, 47 (1904).

[4] Masson, I., Gilbert, L. F., and Buckley, H., *J. Soc. Glass Tech.*, **5**, 337 (1921).

[5] Wood, A. R., *J. Soc. Glass Tech.*, **16**, 43 (1932).

[6] Hunter, R. G., *J. Am. Ceram. Soc.*, **17**, 121 (1934).

[7] Cohn, W. M., *Ann. Physik*, **21**, 761 (1934).

[8] Cohn, W. M., *Glass Ind.*, **17**, 375 (1936).

[9] Bacon, L. R., *J. Franklin Inst.*, **221**, 251 (1936).

study of the boundary corrections in water-glass solutions, and indicated the best experimental conditions.

Stott, Irvine, and Turner[10] measured the rate of fall of a partly counterpoised ball, and Heidtkamp and Endell[11] measured the rate of rise of a ball under a constant force. The apparatus had previously been described by Hänlein[12] and used by Tielsch and Endell.[13] Heidtkamp and Endell also used an apparatus depending on the damping of the oscillations of a suspended platinum ball.

Stott, Turner, and Sloman[14] devised a new method which appeared promising, but which has not been further developed. It is based on the thickness of the film of glass which adheres to a rod of platinum withdrawn from the molten glass at constant rate. The theoretical treatment of the method is uncertain, and hence a calibration factor is necessary, and a knowledge of the surface tension is required. The method is rapid and sensitive, and does not require so large a quantity of glass as to prohibit the use of a platinum containing vessel. This viscosimeter could be adapted to the measurement of surface tension.

The method applicable over the largest temperature range is that of Margules, in which two concentric cylinders are separated by the glass, and the rate of rotation of one of them, usually the inner, is measured under a given torque, the other cylinder remaining stationary. The method has commonly been used as a comparative one, after calibration at low temperatures with a substance of known viscosity. Washburn, Shelton, and Libman[15] found the calibration factor of their apparatus to change with viscosity. The possibility of change of viscosity with rate of shear is discussed subsequently. Other observers have not found a similar effect, but have found that their own results and those of Washburn were in better agreement if it be assumed that the change in calibration factor was an error. English[16] considered the rotating cylinder method the best for viscosities from 10^7 to 10^3 poises, but that the inherent frictional errors rendered it unsuitable for smaller viscosities.

Lillie[17] rotated the outer cylinder and measured the torque on the inner stationary cylinder or spindle, suspended by a torsion member in the center of the fluid, when the cylindrical container was given a uniform angular motion. He at first used a calibration factor, but later[18]

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[10] Stott, V. H., Irvine, E., and Turner, D., *Proc. Roy. Soc. (London), A,* **108,** 154 (1925).

[11] Heidtkamp, G., and Endell, K., *Glastech. Ber.,* **14,** 89 (1936).

[12] Hänlein, W., *Glastech. Ber.,* **11,** 161 (1933).

[13] Tielsch, A., and Endell, K., *Glastech. Ber.,* **12,** 84 (1934).

[14] Stott, V. H., Turner, D., and Sloman, H. A., *Proc. Roy. Soc. (London), A,* **112,** 499 (1926).

[15] Washburn, E. W., Shelton, G. R., and Libman, E. E., *Univ. Ill. Eng. Expt. Sta. Bull.,* **140,** (1924).

[16] English, S., *J. Soc. Glass Tech.,* **12,** 107 (1928).

[17] Lillie, H. R., *J. Am. Ceram. Soc.,* **12,** 505 (1929).

[18] Lillie, H. R., *Phys. Rev.,* **36,** 347 (1930).

modified the method to render it absolute and independent of calibration factor, by determining the correction to be applied for the finite length of the rotating spindle. The apparatus was used for viscosities of from 10 to 10^4 poises by rotating the outer cylinder; from 10^3 to 10^8 poises by turning the outer cylinder through a small angle and timing the aperiodic return of the inner cylinder or spindle.

An additional difficulty in the viscosity range within which the concentric cylinder method is particularly applicable is devitrification. Many common glasses, especially the pure soda-lime glasses of special interest, have their liquidus temperatures within this viscosity range; and the presence of an undetermined amount of solid phase in the liquid not only vitiates the measurements, but also changes the composition of the remaining glass. This difficulty of course will be met with in any method, and can be minimized only by keeping the glass in the temperature range immediately below its liquidus for as short a time as possible.

Viscosities greater than 10^8 poises are measured by observing the rate of deformation of a glass rod under a given force. Some observers have measured the rate of twisting under a known torsion [19]; others, the rate of extension under a known load.[20] At viscosities of about 10^8 poises, Lillie [21] allowed the glass fibers, 0.50 to 0.70 mm. in diameter, to stretch under their own weight; at larger viscosities the fiber was loaded first with 0.14 g., then with 0.94 g., 15 g., 100 g., 500 g. or 1000 g. The results obtained on three glasses, whose compositions are given later (p. 162), are shown in Fig. V. 20.

In addition to the above methods, all of which give measurements of viscosity in c. g. s. units, several methods have been used in which viscosities have been compared with that of a standard glass of unknown viscosity. The experiments of Veseley,[22] of Williams and Cox,[23] and of Lecrenier and Gilard [24] were of this character.

Theoretical Considerations

The theory of liquid viscosity has been developed both from the most general considerations and empirically. It is intimately associated with the constitution of liquids, a problem which is receiving a great deal of attention at present from investigators who have many different points of view. Rapid developments are to be expected in the near future.

[19] Stott, V. H., Irvine, E., and Turner, D., *Proc. Roy. Soc. (London), A*, **108**, 154 (1925).

[20] English, S., *J. Soc. Glass Tech.*, **7**, 25 (1923).

[21] Lillie, H. R., *J. Am. Ceram. Soc.*, **14**, 502 (1931).

[22] Veseley, V., *Sprechsaal*, **44**, 441 (1911).

[23] Williams, A. E., and Cox, S. F., *Trans. Am. Ceram. Soc.*, **18**, 315, 336 (1916).

[24] Lecrenier, A., and Gilard, P., *Bull. Soc. Chim. Belg.*, **34**, 27 (1925).

Eyring[25] discussed viscosity in terms of the general equation for a process by which matter re-arranges by surmounting a potential barrier, and applied the results obtained to glass, especially in the annealing range. Gemant[26] made use of the concept of a complex viscosity to discuss the dielectric losses due to dipole rotation.

The experimental work on viscosity has been discussed by several writers. Le Chatelier[27] proposed a formula $\log \log \eta = Mt - P$ for the viscosity-temperature relation, which of course tends to rectify the curves. But even using a log log curve the experimental data could not be represented by a straight line, and Le Chatelier chose to represent them by two intersecting straight lines, whose intersection was interpreted as representing an allotropic transformation in glass. In a later publication[28] he abandoned this view, but his original paper has been cited as authority for the existence of allotropic forms of glass. Preston,[29] discussing the equation, stated that it "gives imaginary results at most temperatures, and that in its present form it is mathematically inadmissible and physically impossible."

Fulcher[30] gave a critical discussion of the results of English, comparing the difference between the viscosity of each glass with that of the $Na_2O \cdot 3SiO_2$ glass from which it was derived. On plotting these differences, families of curves were obtained which showed well-marked minima, from which Fulcher obtained what he termed "aggregation temperatures" of the glasses. When the term is so defined no objection can be raised, but it is not to be taken as a temperature of equilibrium between, or formation of, different states of aggregation, with which it has no connection. Indeed, it is doubtful if any physical meaning is to be connected with the minima of these different curves.

An interesting discussion of the viscosity of glass has been given by Stott[31] who pointed out that no adequate mechanical theory of the viscosity of liquids exists at present, although the viscosity of a gas can be explained quantitatively on the basis of the kinetic theory. For this reason, it has not been found possible to correlate with any accuracy the viscosity of a liquid with its other physical properties. "No general theory of the internal friction of solids which is not at variance with experiment has yet been proposed in quantitative form. Moreover, great confusion of nomenclature exists which may easily lead to misconception. We have seen that whereas the word viscosity has a very definite meaning when applied to the ordinary mobile

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[25] Eyring, H., *J. Chem. Phys.*, **4**, 283 (1936).

[26] Gemant, A., *Trans. Faraday Soc.*, **31**, 1582 (1935).

[27] Le Chatelier, H., *Compt. rend.*, **179**, 517 (1924); *J. Soc. Glass Tech.*, **9**, 12 (1925).

[28] Le Chatelier, H., *J. Soc. Glass Tech.*, **10**, 99 (1926).

[29] Preston, F. W., *J. Soc. Glass Tech.*, **13**, 19 (1929).

[30] Fulcher, G. S., *J. Am. Ceram Soc.*, **8**, 339 and 789 (1925).

[31] Stott, V. H., *J. Soc. Glass Tech.*, **10**, 424 (1926).

liquids, its meaning becomes increasingly arbitrary as the viscosity of the liquid becomes greater. When the 'solid' state is reached, the differences between the meanings attached to this word are so great that the grossest misconceptions may arise. Reference to a well-known compilation of physical tables tells us, for example, that the viscosity of steel at ordinary temperatures is approximately 10^9 poises. If the definition of viscosity in this case were similar to that used in the present paper, we should be led to suppose that steel at room temperature has a consistency something like that of glass at a temperature of more than 100° above its annealing point. This example has been brought forward because the outstanding feature of the deformation of solids is their extraordinary complexity."

Several authors [32] have derived an equation of the form

$$\frac{1}{\eta} = \phi = Ae^{-k/T}$$

expressing the relation between viscosity or fluidity and temperature. Sheppard derived the formula from a consideration of a distribution following the Maxwell-Boltzman law of "regionally oriented molecules" and free and unordered molecules. The conception of the constitution of liquids assumed by them is expressed by the following quotation from Stewart [33]: "The point of view of this laboratory is that every liquid contains a myriad of small groupings of molecules produced by forces acting between them, the groups being neither perfect in form nor permanent. The word 'cybotaxis' means literally space arrangement, and is adopted to designate this condition in a liquid. We have learned to recognize a crystal as being approximately perfect only in fragments. The liquid goes to a much greater extreme. Its semi-perfect small groups do not even retain their identity. Viscosity is that of groups and of unorganized molecular arrays between them, and this does not depend upon the structure of a single molecule."

Andrade proceeded from considerations not greatly different. "There is for a liquid molecule a vibration about a slowly displaced equilibrium position, with a frequency which is the same as in the solid state. . . . It is further assumed that when, at every extreme vibration, the molecules of one layer come into contact with those of an adjacent layer at this contact they will, in general, enter into a temporary union, the duration of which does not exceed the very brief time necessary for the molecules to acquire a common velocity of translation. The duration of this union must be very small compared to the period of vibration, and

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[32] de Guzmán, J., *Anales soc. espan. fis. quim.*, **11**, 353 (1913). Dunn, J. S., *Trans. Faraday Soc.*, **22**, 401 (1926). Drucker, C., *Z. physik Chem.*, **92**, 287 (1917). Andrade, E. N. da C., *Nature*, **125**, 309, 582 (1930); *Phil. Mag.*, **17**, 497 and 698 (1934). Sheppard, S. E., *Nature*, **125**, 489, 709 (1930); Sheppard, S. E., and Houck, R. C., *J. Rheol.*, **1**, 349 (1930).

[33] Stewart, G. W., *Phys. Rev.*, **32**, 558 (1928).

does not involve anything of the kind that is ordinarily called association."

From the preceding considerations Andrade derived the same expression for the relation between viscosity and temperature. He used the term "crystalline" to express his conception of the transitory groupings which give rise to viscosity, in preference to "cybotactic," and contrasts such groupings with "association." It is doubtful if such differentiation is justified, and it is not necessary. It is probable that the condition is characteristic of all liquids, especially so of non-polar liquids, and that it represents transitory or statistical arrangements the probability of which is the determining factor not only in viscosity but in "association" and "solvation." The use of the term "crystalline" is unfortunate.

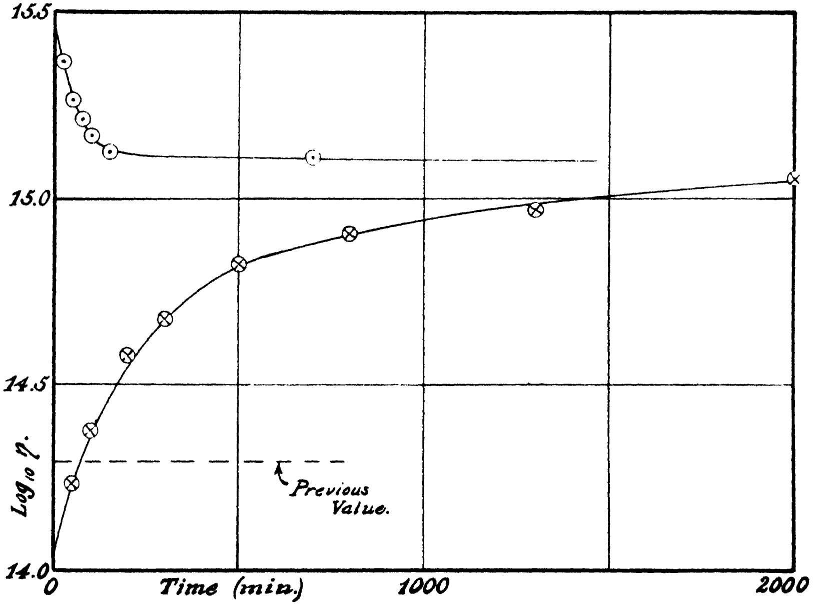

FIGURE V. 1.—Viscosity-Time Curves for Two Samples of a Glass at 486.7° C. The upper curve is for a sample previously heated at 477.8° C. for 64 hours; the lower curve is for a sample in the freshly-drawn condition. After Lillie.

Effect of Time*

Stott, Irvine, and Turner[10] found that several hours were required to reach a constant condition when the viscosity was as high as 16.5 poises. Lillie made a careful study[34] of the change of viscosity with

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* Cf. the discussion on p. 181.

[34] Lillie, H. R., *J. Am. Ceram. Soc.*, **16**, 619 (1933).

time in the annealing range, and found that the time required to reach the constant viscosity characteristic of a given temperature increased as the temperature was lowered. The change in viscosity with time of glass No. 1 is shown by Figs. V. 1 and V. 2. The upper curve in Fig. V. 1 is for a sample previously held at 477.8° for 64 hours, a period sufficient for its viscosity to approach close to the equilibrium value, and the lower curve is for a newly drawn fiber. The initial viscosity for the two samples is different by a factor of more than ten, but that they approach the same final viscosity is evident from Fig. V. 2, in which the reciprocals of the time in minutes are plotted against viscosity. At higher temperatures less time is required; at lower temperatures longer times, until it becomes practically impossible to reach the equilibrium viscosity. The Pyrex resistant glass annealed by Morey[35] for two years probably had not yet reached the equilibrium viscosity, although the strain in the glass was still decreasing.

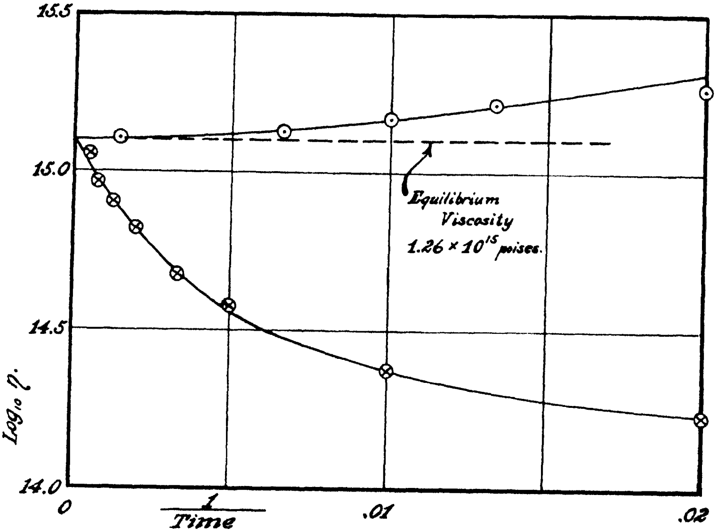

FIGURE V. 2.—The Viscosity Curves of Fig. V. 1 re-plotted with Viscosity against the Reciprocal of Time, to show the Convergence to a Common Value. After Lillie.

In a later study, Lillie[36] followed the change in viscosity with time of chilled fibers at a temperature of 453°. He found that the viscosity was still increasing after 10,000 minutes, although it had already increased 25-fold, from 0.12×10^{16} to 3×10^{16} poises.

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[35] Morey, G. W., and Warren, B. E., *Ind. Eng. Chem.*, **27**, 966 (1935).

[36] Lillie, H. R., *J. Am. Ceram. Soc.*, **19**, 45 (1936).

Change of Viscosity with Rate of Shear

The possible change of viscosity with the rate of shear has been considered by several investigators, but that there is such a change has not been shown. The change in calibration factor found by Washburn, Shelton, and Libman[37] has been taken as indicating such a change. They calibrated their apparatus against liquids which had been measured by the capillary and falling-ball methods. For a given apparatus employing a given height of liquid the fundamental equation may be written $\eta = k(W/S)$ in which W is the mass of the falling weight which rotated the inner cylinder at S revolutions per minute. The ratio η/k should be independent of viscosity, but they found the following values, taken from the points on their curves for the six calibrating liquids: $\log \eta = 0.577$, $\eta/k = 0.76$; 1.554, 1.00; 2.870, 1.26; 3.73, 3.77; 4.12, 1.90; 5.20, 2.95. No explanation of these puzzling results has been offered by them.

Neither English[38] nor Lillie[39] found any similar effect. Lillie, who used large changes in the rates of shear, concluded, "The calibration factor of the concentric cylinders remains constant over the range of viscosities between 5 and 3,500 poises. In any case the deviation from constancy is small." Stott, Irvine, and Turner[10] found the calibration of a falling ball viscosimeter to change 9.2 per cent of its value at 100 poises when the viscosity was increased to 1000 poises; and 10.7 per cent for experiments made by determining the logarithmic decrement of an oscillating cylinder. "It will be seen, then, that in spite of failure to observe a variation of the logarithmic decrement with amplitude, it is probable that the viscosity of syrup does depend on the rate of shear." The ten per cent change in calibration factor observed is of a different order of magnitude from that found by Washburn, Shelton, and Libman. Over the same interval from 100 to 1000 poises their calibration factor, as read from their smooth curves, changed from 1.05 to 2.64, a change of 250 per cent of the value at 100 poises.

The conclusion appears justified that no change of viscosity with rate of shear has been proved, and if it does exist it is less than the error of measurement of any work which has been done on the viscosity of glass.

Plasticity in Glass

All the available evidence indicates that the curves giving the relation between applied force and the resulting deformation pass through the origin, and hence there is no region of plasticity in glass.

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[37] Washburn, E. W., Shelton, G. R., and Libman, E. E., *Univ. Ill. Eng. Expt. Sta. Bull.*, 140 (1924).

[38] English, S., *J. Soc. Glass Tech.*, **8**, 205 (1924).

[39] Lillie, H. R., *J. Am. Ceram. Soc.*, **12**, 505 (1929); *Phys. Rev.*, **36**, 347 (1930).

The careful studies by Lillie[34] appear to demonstrate that, "No indication of a plastic or true solid state was found although viscosities of more than 10^{16} were measured." The apparent decrease which took place in the viscosity whenever a larger weight replaced a smaller one, is probably to be explained by an elastic reaction. Similar but larger effects were observed at higher viscosities. With a glass at a temperature at which its equilibrium viscosity was $10^{15.5}$ poises, a change in the load caused an immediate elastico-viscous elongation, but after some time the elongation curve again became that characteristic of the original loading. "Further, it may be said with fair certainty that at any given time, at least at this temperature, the glass is truly viscous, but might not seem so in actual test unless time is given for the elastic reactions to work themselves out."

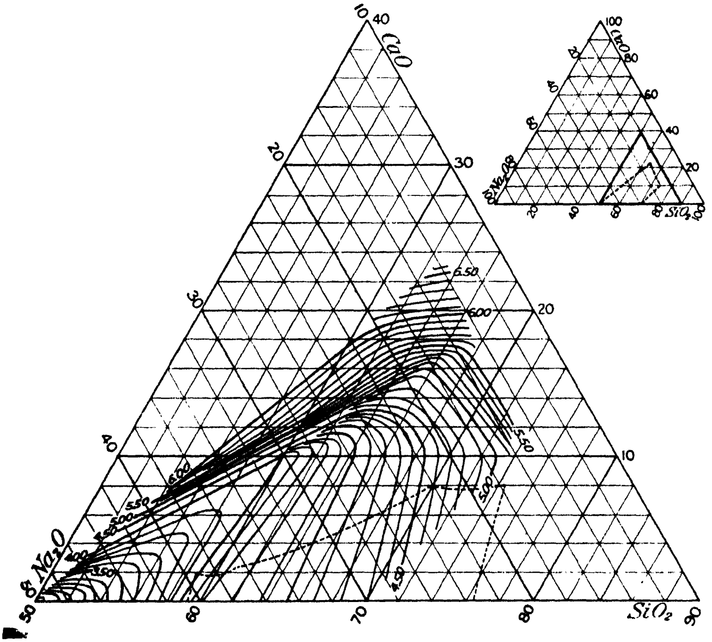

FIGURE V. 3.—Log Isokoms (Lines of Constant Viscosity) in the system Na_2O-CaO-SiO_2 at 900° C. Viscosity in Log Poises, Composition in Percentage by Weight. After Washburn, Shelton and Libman, with sequence of components altered. The Broken Line is the Liquidus Curve at 900°, after Morey and Bowen.

Taylor, McNamara, and Sherman[40] studied the elastico-viscous properties of a glass of the batch composition: SiO_2, 70%; Na_2O, 21%; CaO, 9%; at temperatures in the annealing range. The "transition

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[40] Taylor, N. W., McNamara, E. P., and Sherman, J., *J. Soc. Glass Tech.*, **21**, 61 (1937).

temperature," determined by the thermal expansion method, was 515 ± 5°. The fibers, loaded with a weight of 54.5 g., were annealed by holding them in the furnace at each temperature for about three times as long as the durations of the runs at that temperature. Upon the application of a further load there was an immediate elongation, followed by an elongation the rate of which decreased until it reached a constant value. Upon removal of the load there was an immediate, followed by a slow, contraction. The curves of elongation versus time were separated into three parts: an immediate (five seconds) elastic effect, a delayed elastic effect, and truly viscous flow. The rate of truly viscous flow remained constant, and no change of viscosity with time could be observed. Following are the viscosities so obtained:

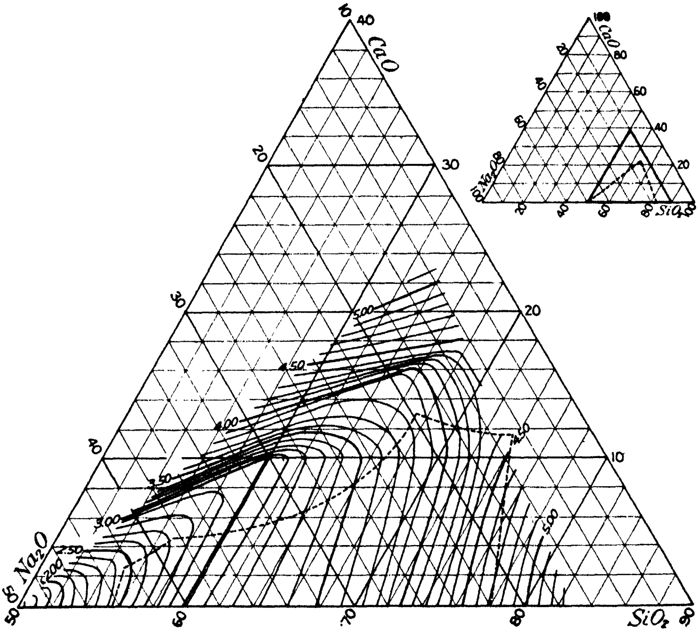

FIGURE V. 4.—Log Isokoms in the System Na_2O-CaO-SiO_2 at 1000° C. After Washburn, Shelton and Libman. The Broken Line is the Liquidus Curve at 1000°, after Morey and Bowen.

Temp. (°C.)	475.0	480.6	491.5	500.0	505.0	510.0	512.5	515.0	525.0
$\eta \times 10^{18}$	113	45.5	8.72	4.36	1.78	0.805	0.770	0.525	0.182

Experimental Results

Washburn, Shelton, and Libman[37] worked with 17 glasses in the ternary system Na_2O-CaO-SiO_2, made by mixing three stock glasses, the compositions of which were determined by analysis. They used the rotating cylinder method, and found the calibration factor to vary with the viscosity, a variation which has not been confirmed by other investigators. Each of the glasses contained from one to two per cent of impurities; the synthetic compositions, not corrected for impurities, are in Table VII. 9. The experimental data are given for only one glass.

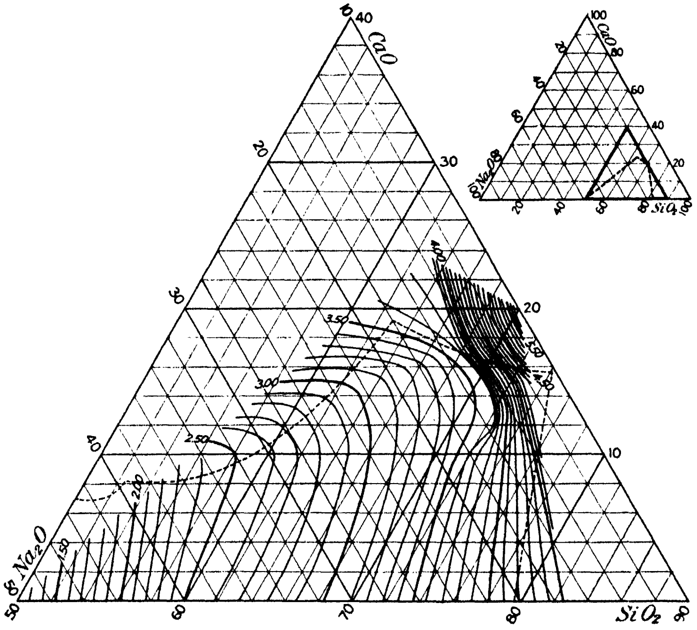

Figure V. 5.—Log Isokoms in the System Na$_2$O-CaO-SiO$_2$ at 1100° C. After Washburn, Shelton and Libman. The Broken Line is the Liquidus Curve at 1100°, after Morey and Bowen.

The interpolated results are given in log η-temperature curves for the various mixtures; in tables of viscosity at rounded temperature intervals interpolated from the log η-temperature curves; and in a series of triangular diagrams which give the curves passing through compositions having the same log viscosity, called log isokoms, at 100° C. intervals from 900° to 1500° C. These triangular diagrams are reproduced in Figs. V. 3 to V. 9* From these curves the log η-temperature curve of any glass included within the composition range can be obtained.

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* The diagrams as reproduced are traced from the original, with sequence of components altered. The broken curves represent the liquidus boundaries for the given temperature, after Morey and Bowen.

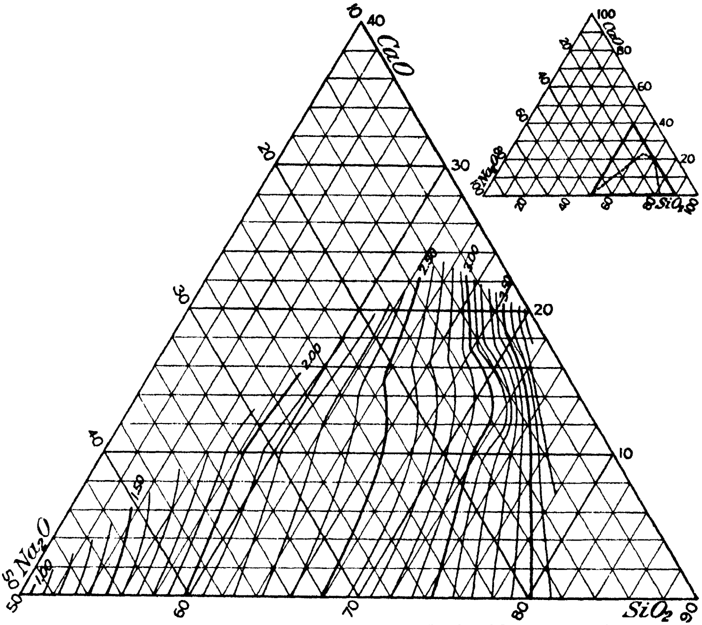

FIGURE V. 6.—Log Isokoms in the System Na_2O-CaO-SiO_2 at 1200° C. After Washburn, Shelton and Libman.

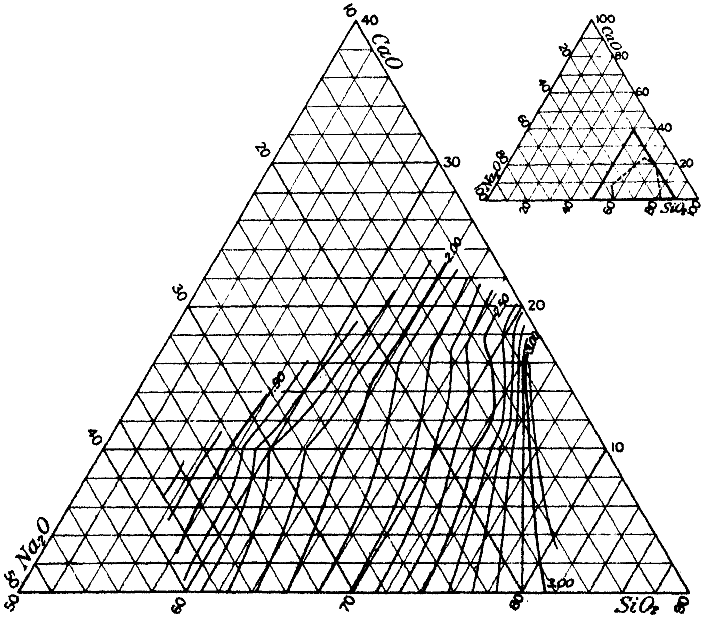

FIGURE V. 7.—Log Isokoms in the System Na_2O-CaO-SiO_2 at 1300° C. After Washburn, Shelton and Libman.

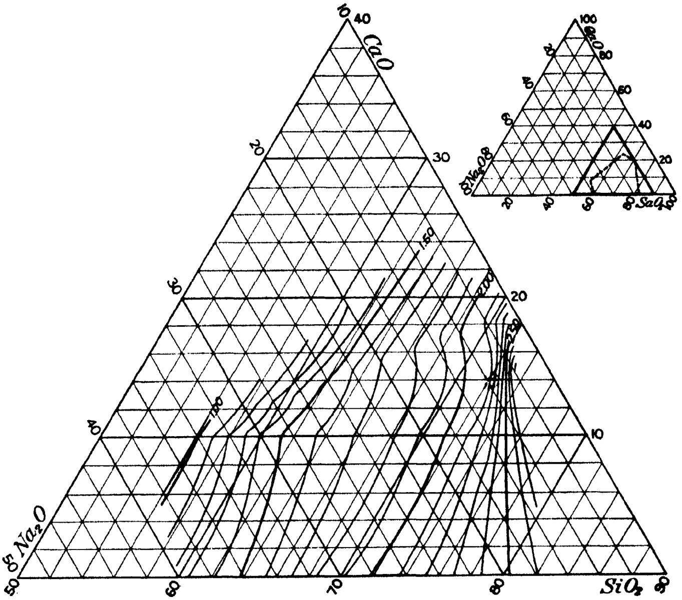

FIGURE V. 8.—Log Isokoms in the System Na_2O-CaO-SiO_2 at 1400° C. After Washburn, Shelton and Libman.

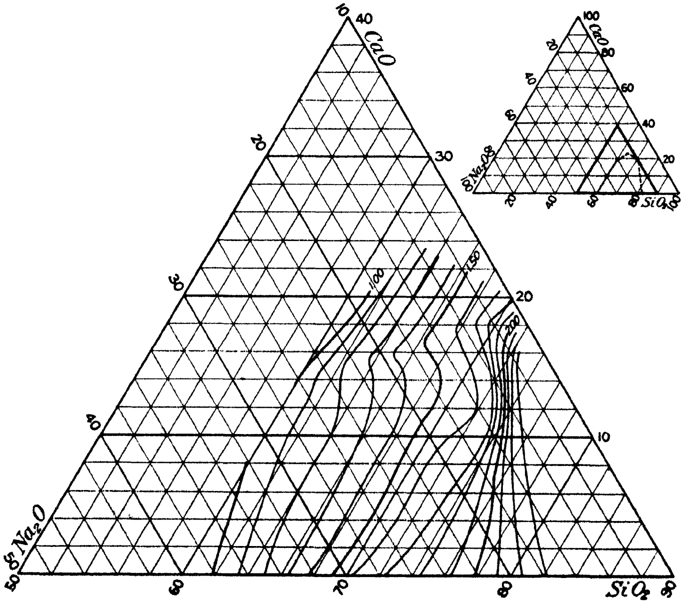

FIGURE V. 9.—Log Isokoms in the System Na_2O-CaO-SiO_2 at 1500° C. After Washburn, Shelton and Libman.

Washburn's results cover a large range of compositions in the soda-lime-silica glasses and are of great value in showing the effect of composition on viscosity. The uncertainty in calibration factor greatly decreases their usefulness. The isokoms at higher temperatures are almost parallel to the Na_2O-CaO side of the composition triangle, indicating that the viscosity is largely determined by the SiO_2 content and that replacement of Na_2O by CaO has no effect on the viscosity. At lower temperatures the isokoms become strongly curved; with low CaO content the viscosity is still determined by the SiO_2, but with more CaO they become parallel to the Na_2O-SiO_2 side of the component triangle, indicating that the viscosity is determined by the CaO content. It is probable that some of the minor curvatures in the shape of the isokoms are due to experimental error, but it is evident that in a three-component system the effect of change in composition can be understood only after systematic variation in all the components, over the composition range under consideration. Linear variation, say along a line of constant SiO_2 content, or any other arbitrary line, may give a wholly erroneous picture of the viscosity-composition relations.

TABLE V. 1—Viscosities of Two Sodium-Silicate Glasses

After English

Glass No. 1—SiO_2 = 74.05%			Glass No. 600—SiO_2 = 79.84%		
Temp. (° C.)	Viscosity	Log Viscosity	Temp. (° C.)	Viscosity	Log Viscosity
485	5.56×10^{12}	12.745	505	6.16×10^{12}	12.790
500	7.81×10^{11}	11.893	555	9.54×10^{10}	10.980
524	1.34×10^{11}	11.127	598	7.35×10^{9}	9.866
550	1.74×10^{10}	10.240	650	3.22×10^{8}	8.508
575	3.85×10^{9}	9.595	992	8.90×10^{3}	3.949
600	7.31×10^{8}	8.864	1100	1.87×10^{3}	3.272
624	2.37×10^{8}	8.375	1194	5.47×10^{2}	2.738
650	6.25×10^{7}	7.796	1315	1.61×10^{2}	2.208
701	5.04×10^{6}	6.702	1410	7.04×10	1.846
745	1.01×10^{6}	6.004			
790	2.71×10^{5}	5.433			
820	1.06×10^{5}	5.025			
920	1.08×10^{4}	4.033			
1028	1.78×10^{3}	3.250			
1136	3.77×10^{2}	2.576			
1240	9.6×10	1.982			
1310	7.7×10	1.886			

Washburn and Shelton[41] also determined the viscosity-temperature curves of a number of optical glasses. No details are given in the brief note published, and the results are in curve form only. The experiments were criticized by English.

English[42] has determined the relations between composition, temperature and viscosity from the annealing temperatures to the melting tem-

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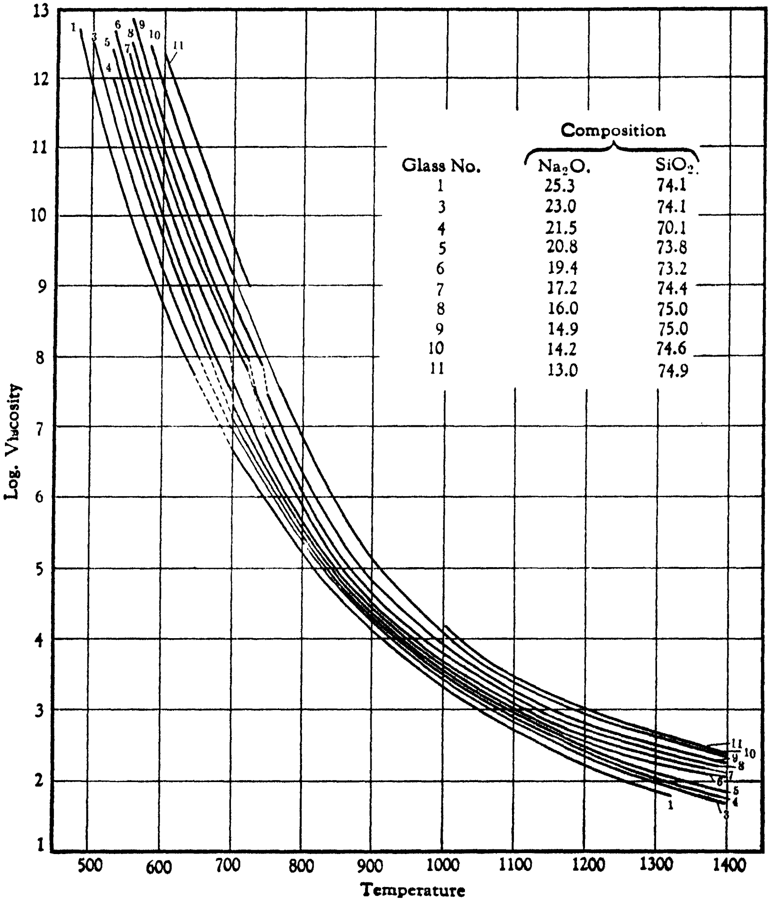
[41] Washburn, E. W., and Shelton, G. R., *Phys. Rev.*, **15**, 149 (1920).

[42] English, S., *J. Soc. Glass Tech.*, **7**, 25 (1923); **8**, 205 (1924); **9**, 83 (1925); **10**, 52 (1926).

peratures in an extensive series of glasses. The results at higher temperatures were determined by the rotating cylinder method, at lower temperatures by the rate of elongation of rods. Unfortunately the two series did not overlap, and there was in this region of intermediate temperatures a marked tendency toward devitrification in many cases. Stott has pointed out that English's results at lower temperature are three times too great, because of a confusion of the coefficient of viscosity with the coefficient of viscous traction.[43]



Glass No.	Composition Na$_2$O.	SiO$_2$.
1	25.3	74.1
3	23.0	74.1
4	21.5	70.1
5	20.8	73.8
6	19.4	73.2
7	17.2	74.4
8	16.0	75.0
9	14.9	75.0
10	14.2	74.6
11	13.0	74.9

FIGURE V. 10.—Change in Log Viscosity, in Poises, of Some Glasses of the Formula $(2 - x)$ $Na_2O + xCaO + 6SiO_2$. After English.

English worked with several series of glasses each of which was

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[43] Trouton, F. T., *Proc. Roy. Soc. (London)*, **77**, 426 (1906).

derived from a Na_2O-SiO_2 glass by substituting another oxide for Na_2O, maintaining the molecular ratio of SiO_2 to other oxides constant. The compositions of the two parent glasses are given in Table X. 3 under Nos. 1 and 600; No. 1 was approximately $Na_2O \cdot 3SiO_2$; No. 600, $Na_2O \cdot 4SiO_2$. The viscosities and log viscosities of these two are shown

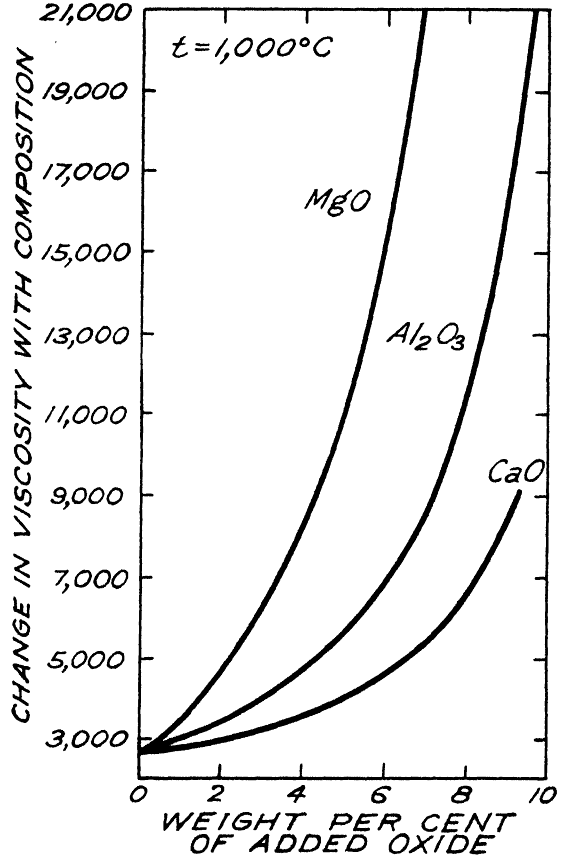

FIGURE V. 11.—Effect on the Viscosity, in Poises, at 1000° C. of Molecular Replacement of Na_2O by CaO, MgO, or Al_2O_3 in the Glass $2Na_2O \cdot 6SiO_2$. After English.

in Table V. 1, and in Figs. V. 10 and V. 14, respectively. In glass No. 600, devitrification took place below 992°, making impossible the study by the rotating cylinder method to a low enough temperature to connect with the determinations by the rate of stretch; but the gap with No. 1 is small and the continuity between the two curves is excellent.

The first series of glasses was derived from No. 1 by replacement of

TABLE V. 2—Relative Rates of Setting* of Some Experimental Glasses

After English

Glass No.	Per cent CaO	Relative Rate of Setting
1	0.21	1.
3	2.61	1.4
4	3.81	1.7
5	4.50	2.0
6	6.26	2.5
7	7.45	3.9
8	8.16	6.5
9	9.36	11.7
	MgO	
26	2.49	1.5
29	5.09	3.0
32	7.46	3.9
390	9.30	5.6

Glass No.	Per cent Al_2O_3	Relative Rate of Setting
443D	6.85	1.4
446C	12.09	1.8
	B_2O_3	
601	4.46	1.17
602	8.28	1.31
603	11.34	1.55
604	14.45	1.78
605	18.84	1.93
606	28.83	2.27
607	39.99	2.62

* The rates of setting are the ratios of the difference in viscosity between 750° and 1050° to the same differences in the parent Na_2O-SiO_2 glasses.

Na_2O by CaO; the compositions of these glasses are given in Table X. 3, and the log viscosity-temperature curves are shown in Fig. V. 10.

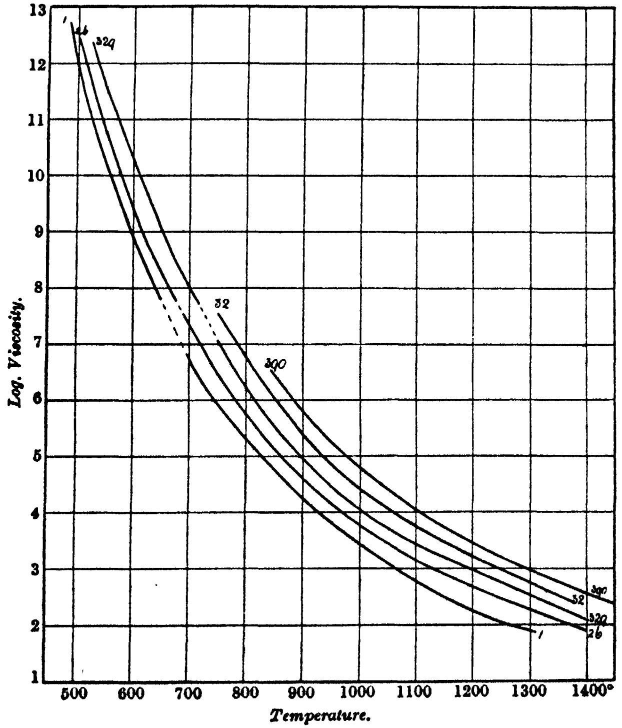

FIGURE V. 12.—Change in Log Viscosity, in Poises, with Temperature of Some Glasses of the Formula $(2 - x)\,Na_2O + xMgO + 6SiO_2$. After English.

Replacement of Na_2O by CaO resulted in a continuous increase in viscosity at every temperature. Curve "CaO" of Fig. V. 11 shows this continuous increase in viscosity with CaO content at 1000°. Since the curves of Fig. V. 10 are not parallel but are somewhat constricted from 1000° to 1100° it follows that the increase in viscosity caused by any particular substitution is not constant throughout the temperature range. The shapes of various viscosity curves may be roughly compared by means of the "relative rate of setting," defined as the ratio of the difference in viscosity of the glass in question between 750° and 1050° to the same difference in the parent Na_2O-SiO_2 glass. Table V. 2 shows the relative rates of setting for several series of glasses studied by English; No. 1 is the parent glass in the series containing CaO, MgO, or Al_2O_3; No. 600 in the series containing B_2O_3.

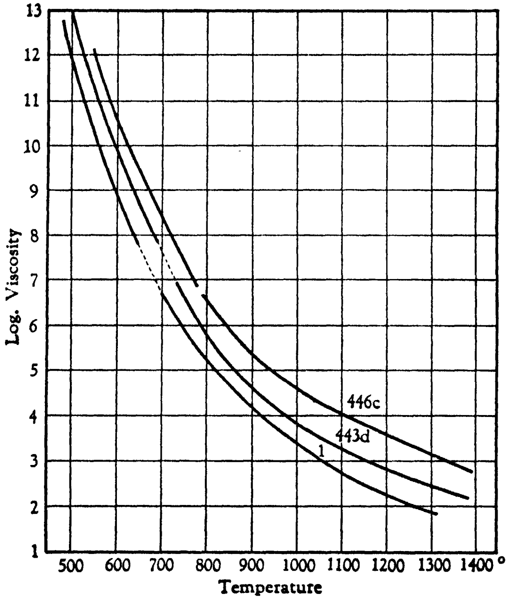

FIGURE V. 13.—Change in Log Viscosity, in Poises, with Temperature of Some Glasses of the Formula $(2 - x)\ Na_2O + xAl_2O_3 + 6SiO_2$. After English.

Fig. V. 12 shows the log viscosity-temperature curves of a number of glasses derived from the same Na_2O-SiO_2 glass (No. 1, Table X. 3) by substitution of MgO for Na_2O. The composition of the glasses is given in Table X. 4, and the relative rates of setting are shown in Table V. 2. These curves are separated farther at the high temperature end than was the case with the curves of the CaO series, and the constriction noted in the CaO glasses from 1000° to 1100° is not present. The change in viscosity on addition of MgO at constant temperature is shown in Fig. V. 11, and it is evident that the addition of MgO results in a more rapid rise in viscosity than does the addition of either CaO or Al_2O_3.

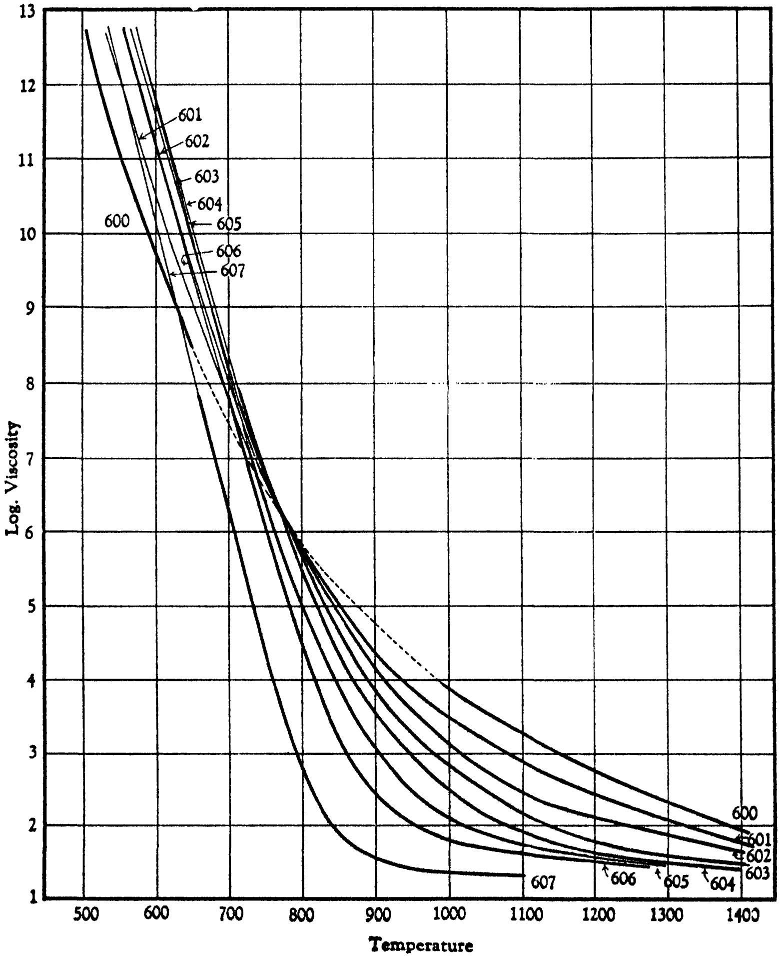

FIGURE V. 14.—Change in Log Viscosity, in Poises, with Temperature of Some Glasses of the Formula $Na_2O + xB_2O_3 + (4 - x) SiO_2$. After English.

Fig. V. 13 shows the log viscosity-temperature curves of the glasses resulting from the replacement of Na_2O by Al_2O_3 in the same original Na_2O-SiO_2 glass. The compositions of the glasses are given in Table X. 3, the change in viscosity at constant temperature, in Fig. V. 11, and the relative rates of setting are shown in Table V. 2. At high temperature, equimolecular substitution of Al_2O_3 increased the viscosity more than either CaO or MgO, but at 1000°, as shown in Fig. V. 11, it was intermediate in its effect. In other words, the effect of alumina is to flatten the viscosity-temperature curve.

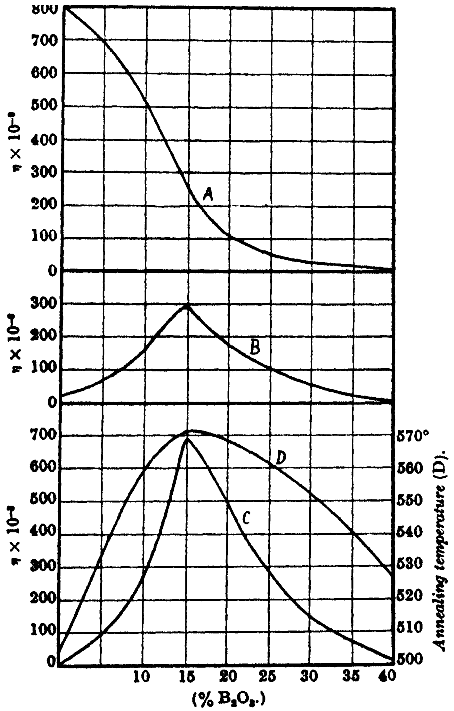

FIGURE V. 15.—Change in Viscosity, in Poises, and Annealing Temperature, with B_2O_3-Content, of Some Glasses of the Formula $Na_2O + xB_2O_3 + (4 - x)SiO_2$. Curve A is at 800° C.; Curve B, at 700° C.; Curve C, at 600° C. After English.

Fig. V. 14 shows the effect of molecular replacement of SiO_2 by B_2O_3, the original glass in this case being No. 600 in Table X. 3, more silicious than the glass used in the preceding cases. The compositions of the glasses are given in Table X. 3, and the relative rates of setting in Table V. 2. There is a pronounced difference in shape between the log viscosity-temperature curves obtained with B_2O_3 and those obtained with CaO, MgO and Al_2O_3. At high temperatures the B_2O_3 greatly reduced the viscosity, and the greater the amount of B_2O_3 added the greater the reduction in viscosity. At lower temperatures, however, this parallelism between the amount of B_2O_3 added and the reduction in viscosity no longer held; substituting B_2O_3 for SiO_2 caused first a rise in viscosity at constant temperature, followed by a diminution in viscosity. The effect of temperature in altering the shape of the viscosity-composition curve is well shown by Fig. V. 15, which shows the change at 800°, 700° and 600°. Curve D in this figure shows the change in annealing temperature with B_2O_3 content. It was suggested by English that such curves may indicate the formation of a compound, unstable at high temperatures, but present to a large degree at lower temperatures.

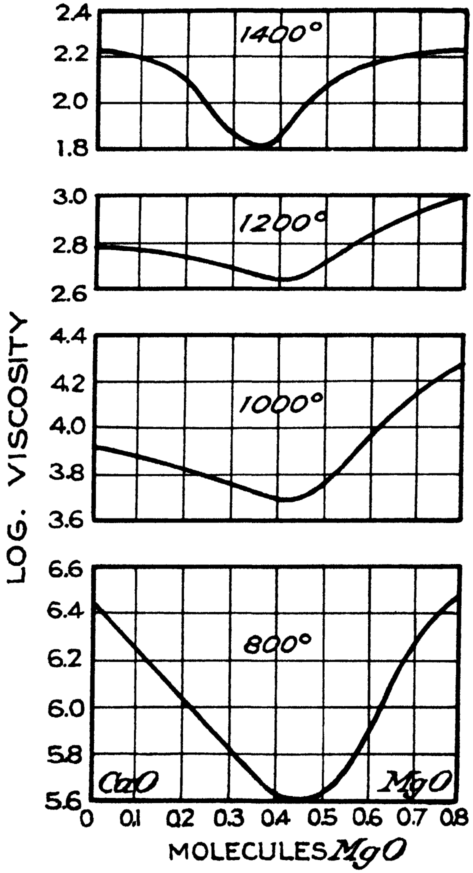

Figure V. 16.—Effect on Log Viscosity, in Poises, of Replacing CaO by MgO in a Glass of the Composition $1.2Na_2O + 0.8CaO + 6SiO_2$. After English.

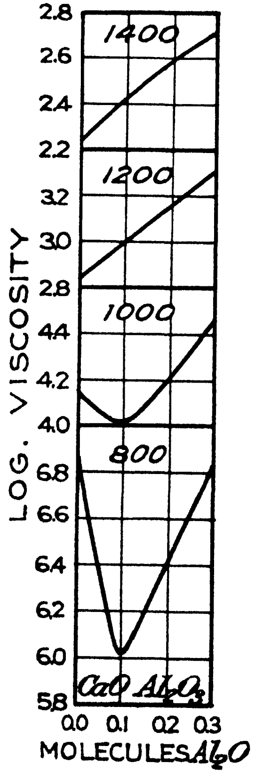

Figure V. 17.—Effect on Log Viscosity, in Poises, of Replacing CaO by Al_2O_3 in a Glass of the Composition $1.1Na_2O + 0.9CaO + 6SiO_2$. After English.

A group of four-component glasses[44] was obtained by replacing CaO by MgO or Al_2O_3 in one of the N_2O-CaO-SiO_2 glasses. The magnesia glasses were obtained from the glass 1.2 Na_2O, 0.8 CaO, 6SiO_2 by stepwise molecular substitution of MgO for CaO. The compositions of the resulting glasses are shown in Table X. 3. The two three-component end members of the series had nearly the same viscosity at each end of the temperature range, but at intermediate temperatures the MgO glass was the more viscous, whereas the mixed glasses were all less viscous. The effect of MgO in reducing viscosity is shown by Fig. V. 16, giving, at constant temperature, the log viscosity-composition of the mixed glasses. There is a well-marked minimum.

TABLE V. 3—Modifications of Viscosity Caused by Substitution

After English

Replacement of	1400°	1300°	1200°	1100°	1000°	900°	
1% Na_2O by 1% SiO_2	+0.040	+0.052	+0.072	+0.083	+0.101	+0.120	
1% Na_2O by 1% CaO	+0.080	+0.070	+0.062	+0.056	+0.052	+0.048	9% CaO
1% MgO by 1% CaO	+0.097	+0.052	+0.000	+0.022	+0.007	−0.052	1.5% MgO
1% Al_2O_3 by 1% CaO	−0.034	−0.024	+0.010	+0.025	+0.090	+0.20	2% Al_2O_3

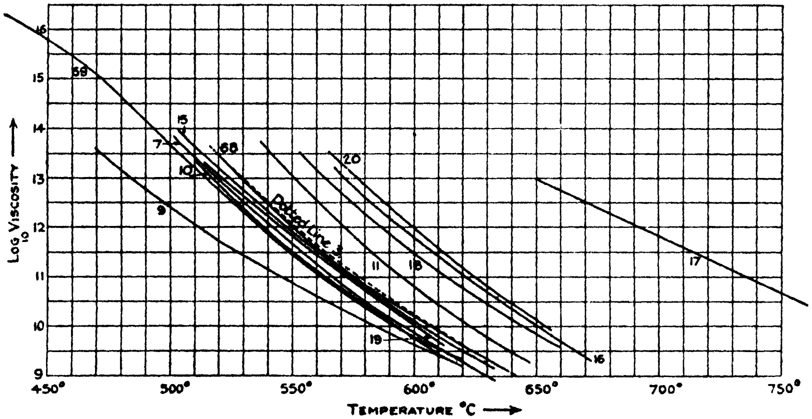

FIGURE V. 18.—Change in Log Viscosity, in Poises, with Temperature in Some Glasses of Compositions Given in Table V. 4. After Stott, Irvine and Turner.

The four-component glasses containing alumina were prepared from the glass: 1.1 Na_2O, 0.9 CaO, 6SiO_2, by the replacement of 0.1, 0.2, and 0.3 molecule of CaO by Al_2O_3. The viscosity-temperature curves of glasses containing alumina were practically parallel and the glasses set less rapidly than the parent soda-lime glass. The effect of substitution of alumina for lime is shown in Fig. V. 17, in which it is brought out

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[44] English, S., *J. Soc. Glass Tech.*, 9, 83 (1925).

that at 1400° and at 1200° there was an immediate and continuous increase in viscosity on substitution of alumina, but at 1000°, and still more at 800°, the viscosity first fell to a minimum, then rapidly increased. At the annealing temperature it is probable that the type of curve obtained will differ from the preceding ones, because the annealing temperatures of the glasses containing alumina are practically the same, and lower than that of the parent soda-lime glass.

English deduced from his measurements[45] a series of factors for correcting viscosities for slight deviations in composition, and for the presence of small amounts of impurities. These factors and their limits of applicability are given in Table V. 3.

The work of Stott, Irvine, and Turner[10] and of Stott, Turner, and Sloman[46] covered much the same temperature range as that of English, but did not include so extensive a composition range as that of either English or Washburn and Shelton. Fig. V. 18 shows the temperature-log viscosity curves of a series of glasses, of composition given in Table V. 4, and Fig. V. 19 shows the log isokoms at 575° in a portion of the ternary system Na_2O-CaO-SiO_2. These curves differ in shape from Washburn's isokoms at 900°, and it will be of interest to learn if the difference is entirely due to the difference in temperature.

TABLE V. 4—Compositions of Glasses Used by Stott

No.	SiO_2	B_2O_3	Na_2O	K_2O	MgO	CaO	ZnO	MnO	Al_2O_3	Fe_2O_3	
9	52.54		0.18	12.10	0.15	0.30		0.16	0.34	0.38	(*1*)
10	65.96		15.74	5.72	0.93	6.04		0.10	4.98	0.78	
11	67.60	2.28	14.24	0.18	0.34	6.24	5.59	0.10	3.40	0.26	
15	66.22		15.46	3.46	0.28	6.40		0.38	7.10	0.48	
16	66.78	8.54	13.38	0.30		0.40		0.36	9.70	0.50	
17	69.82	4.48	3.69	2.06	0.48	8.30			5.34	0.54	(*2*)
18	66.26	7.91	11.66	0.30		0.42	7.30		5.48	0.64	
19	63.26	20.78*	9.10	0.98	0.27	0.74		0.24	3.44	0.20	(*3*)
20	70.72		12.40	0.30	0.41	13.78		0.16	1.86	0.26	
St. 59	66.66	0.32*	15.50	5.58	1.08	6.30			4.33	0.23	
St. 7	66.50		14.00	6.72	0.19	7.18		0.05	5.22	0.16	
St. 3	66.78		11.76	8.18	0.38	7.16		0.10	5.22	0.24	
St. 68	66.50	1.09	15.64	2.90	0.40	6.00		0.30	6.85	0.29	

* By difference. (*1*) Also contains PbO, 33.82; (*2*) Also contains BaO, 548; (*3*) Also contains Sb_2O_3, 0.99.

In a later paper,[47] using a method of great sensitivity, results were obtained at about 1200°, with glasses which had been held some time near to, but below that temperature. "At temperatures below 1200°, it appears that the glass is capable of existing in at least two states, resulting in considerable variations in viscosity. The mean viscosity in this case is that which would be anticipated from an extrapolation of the curve from temperatures above 1200°. In certain circumstances it is possible to obtain the glass at temperatures below 1200° in an

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[45] English, S., *J. Soc. Glass Tech.*, **10**, 52 (1926).

[46] Stott, V. H., Turner, D., and Sloman, H. A., *J. Soc. Glass Tech.*, **9**, 207 (1925).

[47] Stott, V. H., Turner, D., and Sloman, H. A., *Proc. Roy. Soc. (London) A*, **112**, 499 (1926).

unstable state similar to its state at high temperatures. In this case, the viscosity-temperature curve is continuous, and of the same precision throughout." This phenomenon needs further study.

Gehlhoff and Thomas[48] studied the effect of change in composition on viscosity from the annealing range to melting temperatures. The glasses used were not analyzed, but compositions were calculated from the batch melted. The results were given in curves of too small a scale to make possible precise interpolation. In the annealing range several methods were employed: (1) determination of the temperature at which a glass rod under a load of fixed weight and at a definite rate of heating sagged a certain amount; (2) determination of the annealing temperature by observing the temperature at which strain disappeared in a small rod of glass heated at a uniform rate; (3) determination of the temperature of maximum heat absorption by means of a heating curve; (4) determination of the temperature at which the temperature

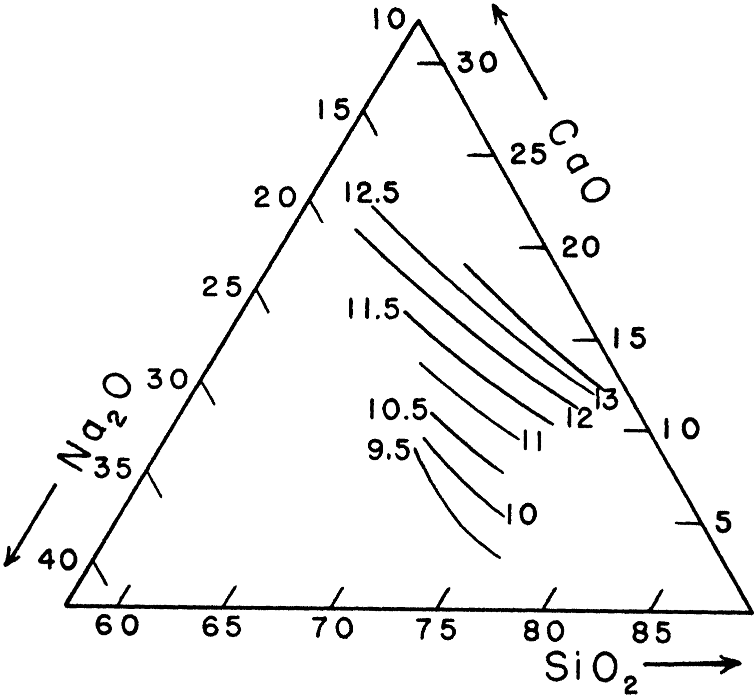

FIGURE V. 19.—Log Isokoms (Lines of Constant Viscosity) in Poises, in the System Na_2O-CaO-SiO_2 at 575° C. After Stott.

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[48] Gehlhoff, G., and Thomas, M., *Z. tech. Physik*, 7, 260 (1926).

coefficient of electrical conductivity at a given rate of heating underwent a sudden change. None of these arbitrary points is necessarily a measure of viscosity, but merely shows the effect of change of composition. In the "viscous range," beginning about 100° above the annealing temperature, two methods were employed: (1) determination of the temperature at which a vertically hanging rod of a given size stretched under the action of a definite load when heated at a definite rate; (2) determination from a heating curve of the temperature of a second absorption of heat, corresponding to a sintering of the powdered glass.

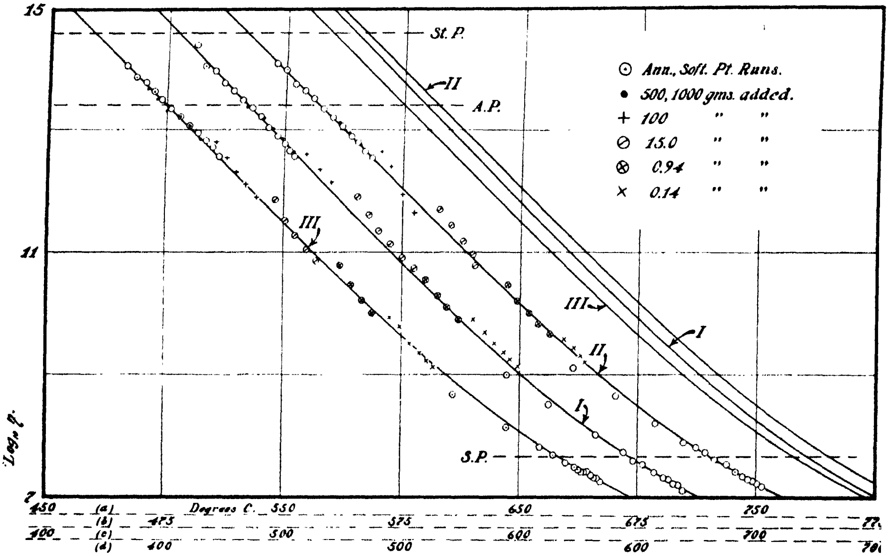

FIGURE V. 20.—Viscosity in Poises of Three Glasses at Low Temperatures. After Lillie.

Neither of these methods corresponds to an absolute measurement. At higher temperatures the viscosity was determined by a modification of the rotating cylinder method. Most of the glasses used were derived from 0.18 Na_2O, 0.82 SiO_2 by replacement of SiO_2 by CaO, PbO, MgO, ZnO or Al_2O_3. The conclusions which were drawn are: (1) alkalies decrease viscosity more than any other oxide, especially at high temperatures, and Na_2O more than K_2O; (2) Na_2O-K_2O glasses have a minimum viscosity in certain proportions, which minimum is particularly noticeable at lower temperatures; (3) MgO and ZnO increase the viscosity, especially at lower temperatures; (4) CaO raises viscosity more than any other oxide at low temperatures, but at higher temperatures it first decreases, then increases, viscosity; (5) BaO and PbO decrease the viscosity at all temperatures; (6) addition of B_2O_3 up to 15 per cent increases viscosity but further addition diminishes it, the effect being much greater at low temperatures; (7) Al_2O_3 increases and Fe_2O_3 decreases viscosity. In considering these results, it must be remembered that they represent variation in composition along arbitrary straight lines in three- and four-component systems, and conclusions drawn therefrom as to specific effects of any component may be in error when extended to variation along some other line. The results are probably of less accuracy than those of Washburn, English, Stott or Lillie.

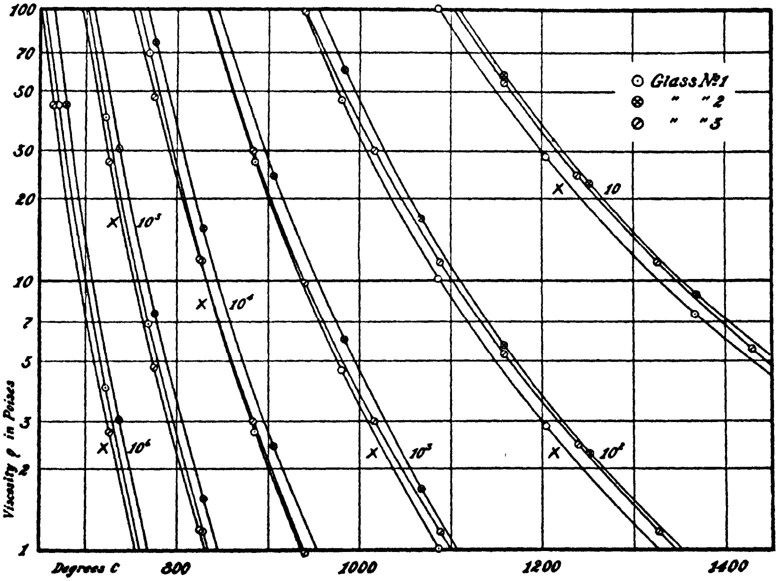

Figure V. 21.—Viscosity in Poises of Three Glasses at High Temperatures. After Lillie.

Lillie has made a thorough study of the change in viscosity with temperature and with time, and his results probably are the most accurate in the literature. In his first papers[49] he calibrated his apparatus, of the concentric cylinder type, with low-melting liquids whose viscosities had been measured by other methods. The results were in good agreement with those obtained by Stott, Irvine and Turner by the falling ball method on a glass of similar composition; in fair agreement with the results of English, although the curves had slightly different slopes; and not in good agreement with the results of Washburn, Shelton and Libman.

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[49] Lillie, H. R., *J. Am. Ceram. Soc.*, **12**, **505** and **516** (**1929**).

In a later paper Lillie[50] modified the Margules method to give absolute values (cf. p. 137). Measurements were made on three glasses,[51] of the following compositions:

	1 %	2 %	3 %
SiO_2	69.73	71.38	71.95
Na_2O	20.96	19.34	20.77
K_2O	Trace	Trace	0.10
CaO	9.05	8.89	6.78
R_2O_3	0.18	0.24	0.10

The results obtained by the Margules method for the three glasses are shown in Fig. V. 20. At lower viscosities fiber deformation methods were used (cf. pp. 138, 161) with the results shown in Fig. V. 21. The ranges of the measurements by the two methods overlap sufficiently to show that the curves obtained are continuous. The complete viscosity curve for Glass 1 is in Fig. V. 22.

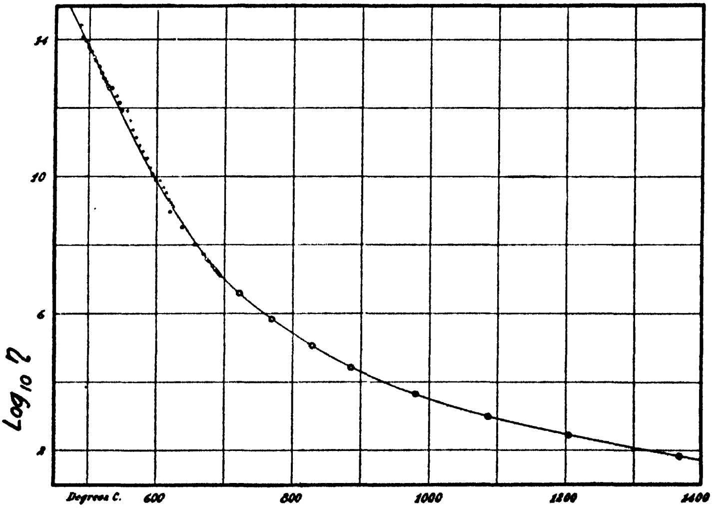

FIGURE V. 22.—Change in Log Viscosity, in Poises, Over a Large Range of Temperature. After Lillie.

Proctor and Douglas[52] also used the rotating cylinder method, and found the calibration factor to remain constant over the range from 10^2 to 10^8 poises. The results for the one glass are reproduced in Fig. V. 23; on the same figure are given the composition of the glass,

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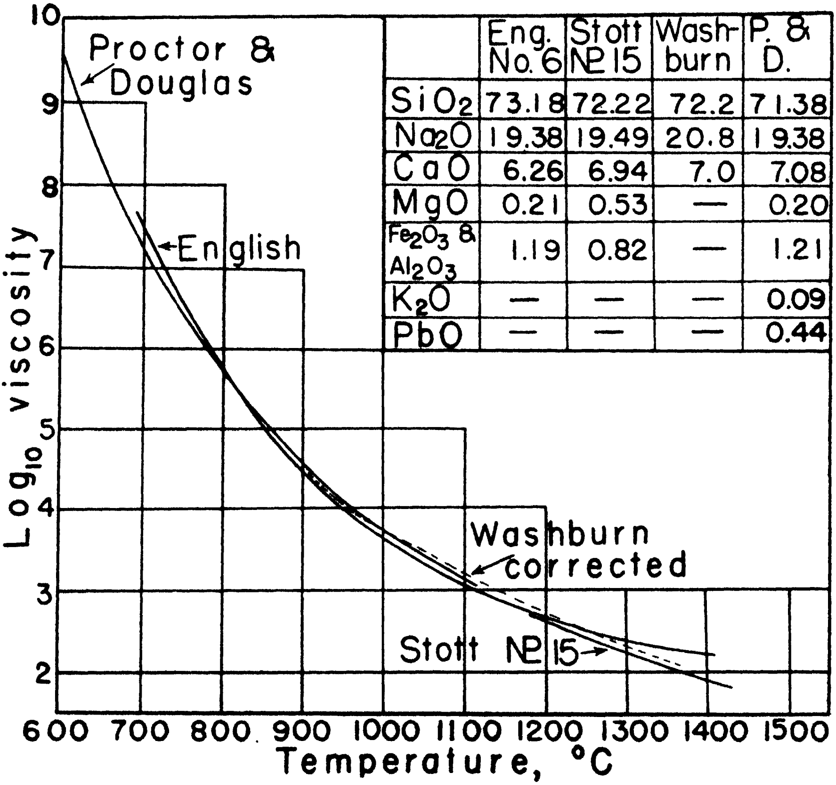
[50] Lillie, H. R., *Phys. Rev.*, **36**, **347** (**1930**).

[51] Lillie, H. R., *J. Am. Ceram. Soc.*, **14**, **502** (**1931**).

[52] Proctor, R. F., and Douglas, R. W., *J. Soc. Glass Tech.*, **13**, **194** (**1929**).

and also the compositions of similar glasses measured by English, by Stott and by Washburn. The curve designated "Washburn corrected" refers to the results of Washburn discussed above, corrected by assuming a constant calibration factor. Proctor and Douglas considered it probable that the change in factor with viscosity found by Washburn, Shelton and Libman was caused by a skin formed over the surface of the syrup used in the calibration, which soon was dragged down when the cylinder was introduced.



	Eng. No. 6	Stott № 15	Washburn	P. & D.
SiO_2	73.18	72.22	72.2	71.38
Na_2O	19.38	19.49	20.8	19.38
CaO	6.26	6.94	7.0	7.08
MgO	0.21	0.53	—	0.20
Fe_2O_3 & Al_2O_3	1.19	0.82	—	1.21
K_2O	—	—	—	0.09
PbO	—	—	—	0.44

FIGURE V. 23.—Comparison of Curves of Log Viscosity, in Poises, Obtained by Different Observers. After Proctor and Douglas.

Babcock[53] used a modified Margules apparatus,* adapted to the simultaneous measurement of electrical conductivity. The apparatus was calibrated by means of two soda-lime-silica glasses previously measured by Lillie; the viscosities of glasses 2BS, 4BS, 1LB, and

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[53] Babcock, C. L., *J. Am. Ceram. Soc.*, 17, 329 (1934).

* See page 137.

TABLE V. 5—Viscosities of Glasses Measured by Babcock

Glass No. 1

° C.	log η
967	1.843
1052	1.387
1108	1.240
1129	1.086
1169	1.004
1176	0.949
1253	0.785
1273	0.703
1360	0.541

Glass No. 2

° C.	log η
817	4.190
842	3.946
915	3.337
946	3.208
973	2.949
997	2.843
1088	2.387
1142	2.259
1149	2.115
1257	1.718
1338	1.471
514	1.347
524	1.286
540	1.225
548	1.163
558	1.145
571	1.088
589	1.020
611	0.865
622	0.829
634	0.804
651	0.795

Glass No. 3

° C.	log η
758	5.098
829	4.417
880	3.940
1013	3.144
1040	3.019
1160	2.532
1209	2.240
1252	2.195
1288	2.019
1318	1.940

Glass No. 4

° C.	log η
814	5.163
871	4.685
928	4.277
939	4.143
1050	3.402
1071	3.305
1166	2.907
1242	2.481
1280	2.451
1316	2.347

Glass No. 5

° C.	log η
1168	3.310
1215	3.099
1220	3.029
1221	3.065
1255	2.912
1262	2.895
1272	2.819
1280	2.819
1317	2.727
1376	2.538

Glass No. 6

° C.	log η
731	6.725
747	6.594
790	5.950
880	4.953
902	4.794
918	4.659
1013	3.883
1101	3.378
1196	2.936
1217	2.807
1337	2.345

Glass No. 7

° C.	log η
737	2.282
742	6.917
747	6.125
824	5.084
839	4.921
848	4.800
950	3.879
971	3.703
1058	3.135
1075	3.065
1162	2.606
1263	2.180
1325	1.959

Glass 1BS

° C.	log η
732	6.835
734	6.776
738	6.738
780	6.026
813	5.503
815	5.524
816	5.524
820	5.348
840	5.190
895	4.531
913	4.406
980	3.743
1042	3.345
1086	3.043
1109	2.988
1112	3.044
1163	2.600
1180	2.561
1182	2.521
1197	2.424
1203	2.575
1250	2.248
1301	2.008
1337	1.882

Glass 2BS*

° C.	log η
1075	1.480
1177	1.304
1237	1.207
1298	1.128
1346	1.058
1410	0.985

Glass 4BS*

° C.	log η
935	1.742
1041	1.388
1145	1.191
1225	1.043
1305	0.894
1387	0.851

Glass 1LB*

° C.	log η
925	1.449
1015	1.214
1124	0.956
1220	0.795
1315	0.681
1390	0.585

Glass 2LB*

° C.	log η
920	2.087
1013	1.778
1115	1.515
1224	1.275
1322	1.131
1394	0.956

Compositions of the above glasses

No.	SiO_2	B_2O_3	Na_2O	K_2O	MgO	CaO	ZnO	PbO	Al_2O_3
1	47.3		52.1						0.3
2	60.0		39.2						0.7
3	65.4		34.0						0.3
4	72.9		26.5						0.7
5	81.0		18.4						0.7
6	72.6	1.43	16.0	0.68	1.7	6.40			1.0**
7	70.12		21.1	tr.		8.77			0.02
1BS	67.3	2.00	14.0			7.0	7.0		2.50
2BS	81	13.00	4.0						2.0
4BS	75	15.00	5.0					5.0	
1LB	65		7.5	7.5				20.0	
2LB	60		5.0	5.0				30.0	

* Measurements by H. R. Lillie.

** R_2O_3.

2LB were determined by Lillie. The compositions and the viscosities are given in Table V. 5.

Heidtkamp and Endell[54] measured the viscosities of Na_2O-SiO_2 mixtures by two methods. For viscosities greater than 6 poises, the time required for a constant force to pull a platinum ball 1 cm. through the liquid was determined, and smaller viscosities were measured by an apparatus depending on the damping of the oscillations of a suspended platinum ball. Both methods required calibration, for which purpose castor oil was used. The results in Table V. 6, which include measurements on technical "water glasses," were interpolated at even temperatures from the temperature-viscosity curves; the values for 1500° were extrapolated. The compositions given in parenthesis were calculated from the batch; the others were determined by analysis and calculated to 100 per cent $Na_2O + SiO_2$. The results were about 40 per cent lower than those of Washburn; but the contamination of Washburn's glasses, especially by Al_2O_3, probably would account largely for the difference. There was no evidence of compound formation to be obtained from the viscosity results.

TABLE V. 6—Viscosity of Glasses in the System Na_2O-SiO_2 from 1000 to 1500° C.

After Heidtkamp and Endell

Weight Per Cent SiO_2	1000°	1050°	1100°	1150°	1200°	1250°	1300°	1350°	1400°	1450°	1500°
88[s]									1080	700	480
83.8						1730	1060	680	450	310	210
79.9		5800	3100	1770	1030	640	410	270	182	128	92
75.5				940	580	370	238	160	110	82	62
75[s]	4600	2500	1360	810	500	310	200	137	96	69	52
69.9	2500	1330	730	440	270	170	112	77	55	39	29
65.8	1490	820	470	285	179	113	77	52	38	28	21
65[s]	1420	760	440	260	166	105	68	46	33	24	18
60.6	570	310	178	110	70	45	30	21	14.6	10.2	7.5
54.4	190	106	63	40	25	16	10.5	7.2	5.0	3.7	2.9
51[s]	43	24	15.5	10.2	7.0	4.7					
49.8		19.4	11.9	8.0	5.5	3.8					
49.2[s]		15.1	9.8	6.6	4.7	3.40	2.50	1.90	1.46	1.17	0.96
48[s]	15.1	9.4	6.0	4.2	3.00	2.30					
44.6	6.3	4.4	3.20	2.23	1.64	1.25	1.00	0.82	0.67	0.56	0.48
39.1			0.95	0.71	0.55	0.44	0.36	0.30	0.26	0.23	0.20

[s] indicates composition by synthesis; all others are by analysis.

The viscosity of CaO-SiO_2 melts containing 54.7, 51.0, and 46.0 per cent SiO_2 was measured in the temperature range from 1450° to 1640°, and there was no indication of a minimum of viscosity at the composition of wollastonite ($CaO \cdot SiO_2$), m. p. 1542°, as found by Herty.[55]

Wadleigh[56] measured the viscosity of some optical glasses from 900° to 1400° by the rotating cylinder method, Table V. 7. In his apparatus

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[54] Heidtkamp, G., and Endell, K., *Glastech. Ber.*, **14**, 89 (1936).

[55] Herty, C. H., Jr., Hartgen, F. A., Heidish, J. A., Metcalfe, K., Norris, F. G., and Royer, M. B., *Carnegie Inst. Tech., Coop. Bull., Mining Met. Invest.*, **47**, (1930).

[56] Wadleigh, W. H., *Bur. Standards J. Research*, **11**, 65 (1933).

the outer cylinder was stationary, and the torque required to rotate the inner cylinder was measured. The measurements were made in porcelain crucibles, which were slightly attacked. The effect of the resulting contamination was studied with a borosilicate glass, using the same porcelain (6A) as was used with the other glasses, and a different porcelain (6B). The effect of volatilization was studied by making melts in platinum (6P). The viscosity results and analyses of the glasses indicated that both sources of error were present.

TABLE V. 7—Viscosity of Some Optical Glasses

After Wadleigh

No.	Viscosity in Poises					
	900°	1,000°	1,100°	1,200°	1,300°	1,400°
1	90,000 ± 2,500	6,600 ± 200	870 ± 35	225 ± 7	87 ± 3	57 ± 1
2	148,000 ± 3,000	20,200 ± 800	3,730 ± 200	1,030 ± 50	360 ± 20	151 ± 4
3	6,600 ± 200	1,525 ± 35	460 ± 25	186 ± 6	88 ± 3	47 ± 1
4		2,040 ± 90	580 ± 20	216 ± 6	105 ± 3	65 ± 4
5		8,000 ± 275	1,500 ± 50	385 ± 15	140 ± 5	76 ± 2
6A*		2,720 ± 175	565 ± 47	199 ± 10	119 ± 3	110 ± 3
6P*		2,000 ± 10	560 ± 11	200 ± 6	90 ± 2	60 ± 1
6B*		2,170 ± 175	560 ± 25	190 ± 5	86 ± 2	51 ± 1

	Approximate Compositions							
	SiO_2	B_2O_3	Na_2O	K_2O	CaO	ZnO	BaO	PbO
1	47.5	4.0		8.5		9.5	30.5	
2	74		12.5	0.2	13.5			
3	41		0.5	6.5				52.0
4	45.5		3.0	5.0				46.5
5	45.5	8.0		8.0			15.0	23.5

* 6A was melted in a porcelain crucible of the same composition as was used for the other melts; 6B in porcelain of a different composition; 6P in platinum.

Frank and Spiridonova[57] studied the effect of temperature and of salt additions on the viscosity of a borosilicate glass, and Frank[58] made similar studies on soda-lime glasses.

Volarovitch[59] described an apparatus of the Margules type, later applied to the measurement of several glasses. Volarovitch and Tolstoi[60] worked on the systems $NaBO_2$-$NaPO_3$ and $Na_2B_4O_7$-B_2O_3, and also measured K_2SiO_3. In the system $NaBO_2$-$NaPO_3$, anomalous results were obtained, which were attributed to plasticity. In the system $Na_2B_4O_7$-B_2O_3, the curves showing the change in viscosity with composition at constant temperature showed maxima at the compositions $Na_2O \cdot 3B_2O_3$ and $Na_2O \cdot 4B_2O_3$, with a minimum between, corresponding to the melting-point curve of Ponomareff,[61] which has been shown to

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[57] Frank, P. E., and Spiridonova, O. N., *J. Opt. and Mech. Ind. (U. S. S. R.)*, **9**, 6 (1934); *J. Soc. Glass Tech.*, **19**, *Abs.* 219 (1935).

[58] Frank, P. E., *J. Applied Chem. (U. S. S. R.)*, **9**, 234 (1936); *C. A.*, **30**, 5007 (1936).

[59] Volarovitch, M. P., *J. Applied Physics (U. S. S. R.)*, **1**, 185 (1928); *J. Soc. Glass Tech.*, **16**, *Abs.* 367 (1932).

[60] Volarovitch, M. P., and Tolstoi, D. M., *J. Soc. Glass Tech.*, **18**, 209 (1934).

[61] Ponomareff, J. F., *Z. anorg. Chem.*, **89**, 383 (1914); *J. Soc. Glass Tech.*, **11**, 39 (1927).

be incorrect by Morey and Merwin.[62] Volarovitch and Tolstoi[63] also made measurements of the viscosity and the electrical conductivity of a soda-lime glass, two slags and a lava. Volarovitch and Leontieva [64] measured silica glass by the elongation method. The results, which were not concordant, showed a viscosity of 10^{13} at about 1200°, 10^{12} at about 1300°, 10^{11} at about 1370°, and 10^{10} at about 1450°.

The possible change of viscosity with long heating, suggested as an explanation of differences observed by practical glass workers, and of supposed differences between batch and cullet melts, was studied by English and Turner.[65] After a series of determinations had been made at temperatures ranging from 1390° to 730°, the temperature was raised to 1200° for 20 hours; a further series of measurements was made down to 900°; the temperature again was raised to 1200°; and the following day another series of determinations was made. No difference was found in the viscosity as the result of this treatment. Furthermore, in a large number of determinations the glass used was remelted in the apparatus, but no difference was noted according as the source of the glass was rod, tubing, or thick slab. Further experiments at lower temperatures, with both soda-lime and lead glasses, showed no variation according to the coarseness of the limestone used in the batch, or in the moisture content of the batch, although in both cases the glass worker found definite differences.

A study with a similar object was made by Gehlhoff and Thomas.[66] They found a correlation between changes in viscosity and in composition sufficient to account for the differences observed between glasses held for a long time in the furnace, and other glasses repeatedly heated and cooled. There is apparently a hiatus between the experimental observations of practical glass workers and the prediction of the glass behavior from viscosity measurements, and more work needs to be done, under the most carefully controlled conditions.

The Viscosity of Slags

Studies have been made on the viscosity of silicate melts of compositions resembling some metallurgical slags by Feild,[67] by Feild and Royster,[68] by Herty and collaborators,[55] and by McCaffery and co-workers.[69] In all these investigations the Margules method of concentric cylinders was used, with the container and the inner cylinder both of

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[62] Morey, G. W., and Merwin, H. E., *J. Am. Chem. Soc.*, **58,** 2248 (1936).

[63] Volarovitch, M. P., and Tolstoi, D. M., *J. Soc. Glass Tech.*, **20,** 54 (1936).

[64] Volarovitch, M. P., and Leontieva, A. A., *J. Soc. Glass Tech.*, **20,** 139 (1936).

[65] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **13,** 70 (1929).

[66] Gehlhoff, G., and Thomas, M., *Glastech. Ber.*, **8,** 77 (1930).

[67] Feild, A. L., *Bull. Am. Inst. Mining Engrs.*, **122,** 307-32 (1917).

[68] Feild, A. L., and Royster, P. H., *U. S. Bur. Mines Tech. Paper*, **187,** (1918).

[69] McCaffery, R. S., Lorig, C. H., Goff, I. N., Oesterle, J. F., Fritsche, O. O., *Am. Inst. Mining Met. Engrs., Tech. Pub.*, **383** (1931).

graphite. Uncertainty was thereby introduced, both from the effect of reduction of silica by carbon at high temperatures, and from the fact that the melts did not wet the cylinders. This introduced a factor not considered in the theory of the method, and an uncertainty in calibration when the calibrating liquid wet the graphite. McCaffery allowed for the melt not wetting the graphite by using a rotating spindle of square cross-section, but failed to prove that the method was theoretically or practically sound.

Feild and Royster studied mixtures in the system $CaO-Al_2O_3-SiO_2$, and found definite maxima and minima directly coördinated with the phase equilibrium diagram. Maxima were found at quintuple points, minima at binary eutectics, an effect which has not been confirmed by other observers in this or in other systems. They also measured the viscosity below their liquidus of melts which crystallize readily, and it is possible that reduction of silica by graphite took place.

Herty and his collaborators did not confirm the results of Feild, especially in the correlation between the viscosity and the melting point. They stated: "The presence of eutectics has no effect on viscosity." They, however, did find a minimum at the composition $CaSiO_3$ in the binary system $CaO-SiO_2$. Heidtkamp and Endell[54] (cf. p. 165) from a careful study of viscosity of melts containing from 46 to 54.7 per cent SiO_2, in the temperature range from 1450° to 1640°, found the curves to be smooth, with no indication of the sharp breaks found by Herty. It is probable that the whole subject of slag viscosity needs critical revision.

There is, however, a very large body of data accumulated on the quaternary system $CaO-MgO-Al_2O_3-SiO_2$, which is presented in the report by McCaffery and co-workers, in the form of numerous diagrams showing the change of viscosity with composition at constant temperatures. The results have little resemblance to those of Feild, and there is no correlation between the viscosity and the phase equilibrium diagram. The effect of magnesia in reducing the viscosity of slags is especially noteworthy.

The Viscosity of Melted Minerals

Several observers have made measurements of the viscosity of silicate mixtures having the composition of minerals. Doelter and Sirk[70] found the viscosity of an impure artificial diopside at 1300° was 33 poises; at 1280°, 106 poises. Bowen[71] from the rate of sinking of olivene crystals, estimated the viscosity of a mixture 30 per cent $CaSiO_3$, 70 per cent $MgSiO_3$ at 1450° to be four poises. McCaffery and his co-workers gave for the viscosity of wollastonite ($CaSiO_3$) at 1650°, 2.38 poises; at 1600°, 2.40 poises; at 1550°, 2.73 poises; of anorthite ($CaO \cdot Al_2O_3 . 2SiO_2$) at

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[70] Doelter, C., and Sirk, H., *Sitzber. Akad. Wiss. Wien*, **120**, 1 (1911); *Monatsh.*, **32**, 643 (1911).

[71] Bowen, N. L., *Am. J. Sci.*, **39**, 175 (1915).

1600°, 25 poises; at 1550°, 38 poises; at 1500°, 60.4 poises; at 1450°, 111 poises; of diopside ($CaMg(SiO_3)_2$) at 1600°, 12 poises; at 1550°, 1.4 poises; at 1500°, 1.85 poises; at 1450°, 3.8 poises; at 1400°, 26 poises.

Kani[72] measured the viscosity by the Margules method of basalt and nepheline basalt. He observed that crystallization took place promptly when the temperature was lowered below a certain value for each rock. The failure to observe this crystallization is a puzzling feature of many studies of silicate melts which are known to crystallize readily. Kôzu and Kani[73] made measurements of melts in the system diopside-albite-anorthite. They found the viscosity of diopside at 1400° to be 80 poises; of anorthite at 1555°, 106.9 poises.

The alkali feldspars have a viscosity of a different order of magnitude. Bowen[74] estimated the viscosity of melted albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) at 1150° to be 10^8 poises; at 1400°, 4×10^4 poises; and of melted orthoclase ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) to be 10^8 at 1250°. Kani[75] found the log viscosity of orthoclase to be 7.0094 at 1400°, 6.6025 at 1450°; of albite, 6.0400 at 1300°, 5.6381 at 1350°, 5.2493 at 1400°, 5.0752 at 1425°. At 1400° mixtures of orthoclase and albite had the following log viscosities: 20 per cent Ab, 6.2264; 40 per cent Ab, 5.8826; 60 per cent Ab, 5.8046; 80 per cent Ab, 5.6576.

Deformation and Transformation Temperatures

In discussing the thermal behavior of glass, the melting point, a characteristic temperature of crystalline substance, is not available, and various empirically defined temperatures, particular points on the viscosity-temperature curves, have been proposed to replace this important constant. To this class belong the deformation temperature, the cohesion point, the softening point and flow temperatures, as defined by various authors. The "annealing temperature," to be discussed in the next chapter, as well as the "transition point," the "lower critical point," the "upper critical point," etc., defined from the shape of the curve of thermal expansion, are temperatures at which the glass, sometimes with a given thermal history, has a characteristic viscosity.

The "deformation temperature" was defined by Weidert and Berndt[76] as the temperature at which the first deformation can be detected in a polished face of a 25-mm. cube, with one diagonal vertical, embedded in kieselguhr. A number of deformation temperatures so obtained are in Table V. 8.

The "cohesion temperature" was defined by Zschimmer[77] as the tem-

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[72] Kani, K., *Proc. Imp. Acad. (Tokyo)*, **10,** 29 and 79 (1934).
[73] Kôzu, S., and Kani, K., *Proc. Imp. Acad. (Tokyo)*, **11,** 383 (1935).
[74] Bowen, N. L., *Trans. Am. Geophys. Union, 15th Ann. Meeting, Pt. I,* 249-255 (1934).
[75] Kani, K., *Proc. Imp. Acad. (Tokyo)*, **11,** 334 (1935).
[76] Weidert, F., and Berndt, G., *Z. tech. Physik,* **1,** 121 (1920).
[77] Zschimmer, E., *Silikat-Z.*, **2,** 129 (1914).

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1600°, 25 poises; at 1550°, 38 poises; at 1500°, 60.4 poises; at 1450°, 111 poises; of diopside ($CaMg(SiO_3)_2$) at 1600°, 12 poises; at 1550°, 1.4 poises; at 1500°, 1.85 poises; at 1450°, 3.8 poises; at 1400°, 26 poises.

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[74] Bowen, N. L., *Trans. Am. Geophys. Union, 15th Ann. Meeting, Pt. I*, 249-255 (1934).

[75] Kani, K., *Proc. Imp. Acad. (Tokyo)*, **11**, 334 (1935).

[76] Weidert, F., and Berndt, G., *Z. tech. Physik*, **1**, 121 (1920).

[77] Zschimmer, E., *Silikat-Z.*, **2**, 129 (1914).

perature at which two polished flat discs of the same kind of glass, placed in optical contact, will coalesce in a given time. The influence of time on the cohesion temperature is shown in Table V. 9; and the cohesion temperatures determined by Zschimmer are in Table V. 8. He adopted a time of 30 minutes as standard, and gave the following as limits for the different glass types:

Table V. 8—Annealing, Deformation, Cohesion, Softening and Flow Temperatures of Some Glasses of Table III. 4

No.	Annealing (*a*)	Deformation (*b*)	Cohesion (*c*)	Softening (*d*)	Flow temperatures (*e*) 30 min.	2 hr.	6 hr.
1	...	570	603	648	...	815	.....
4	...	...	...	...	850	815	755
8	495	605	583	565	810	795	780
20	...	...	505	498	740	725	685
22	...	...	632	640	...	...	...
27	...	...	632	639	910	885	860
28	...	...	484	499	...	...	...
29	...	590	632	642	845	805	785
32	585	645	694	681	845	830	795
35	...	650	674	735	870	835	820
34	565	645	686	681	840	815	800
36	410	460	486	490	730	695	680
38	...	585	547	595	780	730	685
40	390	430	493	491	660	645	630
42	...	...	465	473	...	...	...
44	...	...	457	469	...	...	...

(*a*) After Weidert and Berndt.
(*b*) After Weidert and Berndt.
(*c*) After Zschimmer.
(*d*) After Zschimmer.
(*c*) After Weidert and Berndt.

Cohesion Temperatures of Several Glass Types

Flints	450° - 500°
Silicate crowns	300° - 550°
Borosilicate crowns	350° - 600°
Barium flints	600° - 650°
Barium crowns	600° - 700°

The "flow temperature" of Weidert and Berndt [76] was an attempt to determine the temperature at which "the surface forces counterbalance the viscous forces." It was obtained by holding at various temperatures for a given time a 25-mm. cube of glass embedded in kieselguhr with one diagonal vertical, and by noting when the cube had deformed to

Table V. 9—Change in Cohesion Temperature on Continued Heating

After Zschimmer

	Minutes				Hours		
Time	1	20	50	100	3	14	24
Cohesion Temperature (° C.)	611.3	584.7	574.0	566.8	563.7	553.0	540.0

such an extent that the upper corner could not be detected. The results for a number of glasses with three durations of heating are in Table V. 8.

The softening temperature has been defined in different ways. Zschimmer and Schulz [78] measured the birefringence resulting from sudden cooling of blocks of glass, usually about 4 × 4 × 24 mm., and expressed the relation between the stress S and the temperature t from which the glass was cooled by the equation

$$(t_0 - t)\ (S - S_0) = C,$$

where C, S_0, and t_0 are constants determined experimentally. The constant t_0 is called the "softening temperature." Softening temperatures so determined are given in Table V. 8.

Littleton [79] defined the softening temperature as that at which a thread of glass, 9 inches (22.9 mm.) long and 0.6 mm. in diameter lengthens under its own weight at the rate of one mm. per minute when heated in an electric furnace throughout its upper 9.5 cm. of length. Lillie [51] (cf. p. 162) found that the viscosity at the softening point so defined was 4.5×10^7 poises.

Parmelee and Badger [80] measured the softening temperatures of a series of glasses containing 17.4 per cent Na_2O, 10.1 per cent CaO, and from 72.5 to 62.5 per cent SiO_2, 0 to 10 per cent Al_2O_3. The measurements were made with an interferometer apparatus, and the softening temperatures obtained represented the temperatures at which the interferometer plate (weight about 7 grams) began to deform the three supporting glass pyramids (altitude about 3 mm.). The temperature could be determined within ±2°. The results were represented within the experimental error by the equation

$$t = 582 + 3.2\,p,$$

in which t is the softening temperature, and p is the weight per cent alumina.

Another definition of softening point was included in the following joint recommendation [81] of the Technical Committees of the Deutsche Glastechnische Gesellschaft and of the Society of Glass Technology: "It is agreed that the symbol T_g shall replace all other conventions to denote the transformation temperature of a glass. The maximum point reached on the complete thermal expansion curve for the glass, namely, the point normally corresponding with its softening temperature, shall be denoted by the symbol M_g, and that this symbol shall replace any other convention hitherto in use."

This definition of softening temperature corresponds to a viscosity

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[78] Zschimmer, E., and Schulz, H., *Ann. Physik*, **42**, 345 (1913).

[79] Littleton, J. T., *J. Am. Ceram. Soc.*, **10**, 259 (1927).

[80] Parmelee, C. W., and Badger, A. E., *Glass Ind.*, **17**, 85 (1936).

[81] *J. Soc. Glass Tech., Proc.*, **14**, 159 (1930).

of 10^{11} to 10^{12} poises, and does not correspond to the usual conception of softening as well as does that of Littleton. It does correspond to the viscosity of the extreme upper limit of the annealing range, and has also been called the "incipient softening point," the "upper annealing temperature," denoted by A, and the "upper critical point," designated by C_t. The temperature obtained depends on the thermal history of the glass, and the arbitrary procedure must be followed carefully to obtain concordant results. Littleton's definition leads to more concordant values of the measured softening temperature.

The "transformation temperature," T_g, is discussed under the coefficient of expansion (p. 267). It corresponds to a viscosity of from 10^{13} to 10^{14} poises, depending on the definition and on the method of measurement. It has been called the "lower critical point C."

Chapter VI

The Annealing of Glass

The annealing of glass is a problem of great practical importance, concerning which there is an extensive literature. When glass is cooled without special heat treatment, it is usually in an unequally strained condition which may be harmful because of an increased tendency to breakage, although the effect becomes important only when the strain is great. For most ware what is known as "fine annealing" is neither necessary nor desirable; and for some uses strain is deliberately introduced, in controlled amount and distribution, to decrease the danger of breakage. Optical glass, however, requires the highest type of annealing, and it is in connection with the manufacture of optical glass that the study of annealing has received most attention.

Detection and Measurement of Strain

Strain in glass is detected by its effect on polarized light, an effect which is similar to that of a birefracting crystal. This was discovered in 1813 by Brewster, who found that a glass plate under load behaved as a uniaxial negative crystal, in which the direction of application of the load was the optic axis; and that the birefringence as measured by the path difference between the two plane-polarized light waves formed on traversing the strained block, was proportional to the strain. The birefringence thus serves as a direct measure of the strain, but the relation between stress and strain, the "stress-optical * coefficient," depends on the composition of the glass.

Numerous polariscopes for the detection and measurement of strain have been described. For accurate measurement of strain, either a Babinet compensator or the more sensitive bi-quartz wedge described by Wright,[1] should be used. As a rule the glass samples tested are sufficiently transparent to permit the passage of enough visible light for one to detect the presence of excessive strain, but direct examination is not possible with translucent or semi-opaque glasses. They can be examined by the method devised by Littleton,[2] and used by Mendenhall, Ingersoll, and Johnson,[3] in which either infrared or ultraviolet radiation

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* Cf. the discussion on p. 429.

[1] Wright, F. E., *J. Wash. Acad. Sci.*, **4**, 594 (1914).

[2] Littleton, J. T., U. S. Patent 1,681,991 (1928).

[3] Mendenhall, C. E., Ingersoll, L. R., and Johnson, N. H., *J. Optical Soc. Am.*, **15**, 285 (1927).

is used. The method, which is not affected by roughness or irregularities in the surface, may be applied by means of a photo-cell.

The quantity measured is a difference in refractive index, δ, for the light waves vibrating parallel with and normal to the axis, for the total length of path, l. For unit length of path the birefringence $n_\epsilon - n_\omega = \Delta n/l$. This difference is usually expressed in millimicrons, mμ; 1 mμ = 10^{-6} mm. For optical glass a birefringence of 5 mμ per cm. path is regarded as satisfactory annealing.[4] Adams and Williamson proposed 50 mμ per cm. as a desirable upper limit for plate glass. Twyman[5] proposed that the limit of allowable stress in commercial glass be 1/20 the breaking stress, which would correspond to about 100 mμ per cm. When it is desired to express the strain in terms of stress units, a knowledge of the stress-optical coefficient is necessary. For most glasses a load of 1 kg. per cm.^{2} produces a birefringence of about 3×10^{-7}. A "strain" of 30 mμ per cm. corresponds to $30 \times 10^{-6}/3 \times 10^{-7}$, or 100 kg. cm.^{2}, or about 1400 pounds per square inch.

The Development of Strain in Glass

Experience has shown that to prevent strain, exact control of temperature is important only during a short interval, the "annealing range." Above the upper part of the annealing range, the glass is so fluid that it yields practically instantaneously to stress, and a strain cannot persist. This upper limit is capable of precise practical definition and determination. The lower limit of the annealing range is more indefinite, as the factors of time and dimensions are of such importance that definition is not possible without consideration of their influence. Nevertheless, the lower limit of the annealing range, called the "strain point" by Littleton, is that temperature from which a piece of glass can be quickly cooled without introducing permanent strain. A discussion of the manner in which strain is developed in glass will be instructive.

Suppose that a flat plate or slab of glass, long enough so that end-effects may be neglected, originally free from strain, and at a uniform and comparatively low temperature, is heated on both faces, that is, on the two surfaces normal to the shortest dimensions of the piece. The outside layers become hotter and tend to expand more than the inner layers; that is, the surfaces of the slab are not free to expand the normal amount and will therefore be under longitudinal compression in all directions parallel to the surface of the slab. At the same time the innermost layers will be stretched by the outer layers and will be under tension. The longitudinal stress changes continuously from a compression at the surface to a tension at the middle, necessarily passing through an intermediate zone of zero stress. If the heating be con-

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[4] Wright, F. E., "The Manufacture of Optical Glass and of Optical Systems," U. S. Ordnance Dept., Document No. 2037, Govt. Printing Office, Washington, 1921.

[5] Twyman, F., *J. Soc. Glass Tech.*, **1**, 61 (1917).

tinued until the temperature of the slab again becomes uniform at some temperature well below the annealing range, the stresses caused by the temperature gradient will have disappeared with that gradient. Such stresses may be called temporary, since they continue only so long as the temperature gradient is maintained.

If the sample of glass, of uniform temperature and free from stress, is cooled from the same original condition, temporary stresses will be developed of sign opposite to those resulting from heating; that is, tension in the surface and compression in the middle zone. In general, a temperature gradient established by heating will produce longitudinal compression in the outer layers, and a temperature gradient established by cooling will produce longitudinal tension in the outer layers.

Conversely, if a temperature gradient exists in a slab of glass which is free from stress, the removal of the temperature gradient will cause stresses equal and opposite in sign to those which would be produced by the establishment of the same temperature gradient in a slab free from stress. If the gradient is from a cooler surface to a warmer interior, that is, a gradient established by cooling, the removal of the gradient will produce longitudinal compression in the surface layers, tension in the interior. Such stresses can be permanently removed only by an annealing process, and are called permanent stresses.
low temperatures, at which the relation of stress to strain is that of an

The preceding discussion has been limited to glass at comparatively elastic body. At higher temperatures, the stresses may be gradually relieved, by flow or internal displacement, at a rate which is dependent on the viscosity. At still higher temperatures the stresses may be so evanescent as to escape detection. Suppose that a block of glass is cooled from a temperature at which it yields practically instantaneously to stress, and hence at which temporary stresses are evanescent, and that the rate of cooling of the surface is held constant. Then the temperature distribution within the glass will quickly adjust itself to a parabolic curve, but the establishment of the temperature gradient will not produce any temporary stress because the glass is too fluid to support stress. Let the glass, free from stress but containing a temperature gradient, continue to cool at a rate such that the temperature gradient remains practically constant, until at some low temperature the cooling is stopped and the temperature throughout the block becomes uniform. The removal of the temperature gradient will then produce permanent stress, consisting of compression at the surface, tension in the middle. This experiment, performed by Adams and Williamson, demonstrated that the strain was produced at low temperatures.

If the cooling had been started at some intermediate temperature, such that the establishment of the temperature gradient produced a temporary stress which was only in part released, and the cooling had been continued as before, the slab of glass would contain both a temperature gradient and a part of the stress resulting from the establishment of the gradient. Since the gradient was produced by cooling, the stresses would consist of a tension at the surface, and a compression at the middle. Then when the temperature gradient was removed, part of the resulting compression at the surface would be neutralized by the tension already present, and the permanent stress in the glass would be less than in the preceding case. It has already been shown that if the temperature gradient were established at a temperature at which none of the temporary stress was lost, no permanent strain would result.

From the above reasoning it follows that the stresses in poorly annealed glasses are due to the removal of the temperature gradient at low temperatures, and that the amount of permanent strain is the difference between that caused by the removal of the temperature gradient, which produces a compression on the surface, and the temporary strain carried down from high temperature, which is a tension in the surface layers. In other words, the permanent stress is equal and opposite in sign to the stress lost in cooling.

Adams and Williamson gave a mathematical discussion of the temperature distribution and stresses, and the resulting birefringence, as the result of thermal gradients developed by sudden heating or cooling of glass. This discussion is reproduced in Chapter XIV in connection with the thermal endurance of glass.

The Removal of Strain from Glass

Strain is removed from glass by an annealing process which is designed to remove most or all of the strain at some constant temperature and to cool the glass under such conditions that the product retains no more than a predetermined amount. The rate at which strain is removed from glass has been the subject of several studies, which appeared to lead to puzzling conclusions [6] until the recent work of Lillie [7] reconciled the apparent anomalies.

The rate of removal of strain was discussed by Maxwell,[8] who wrote: "...The phenomena of viscosity in all bodies may be described, independently of hypothesis, as follows:

> "A distortion or strain of some kind, which we may call S, is produced in the body by displacement. A state of stress or elastic force which we may call F is thus excited. The relation between the stress and the strain may be written $F = ES$, where E is the coefficient of

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[6] Preston, F. W., *Glass Ind.*, **15**, 57 (1934). Littleton, J. T., *Ind. Eng. Chem.*, **25**, 748 (1933). Bailey, J., and Sharp, D. E., *J. Am. Ceram. Soc.*, **16**, 367 (1933).

[7] Lillie, H. R., *J. Am. Ceram. Soc.*, **19**, 45 (1936).

[8] "The Scientific Papers of J. C. Maxwell," edited by W. D. Niven, **2**, 30, Cambridge Univ. Press, 1890.

elasticity for that particular kind of strain. In a solid body free from viscosity, F will remain $= ES$, and

$$\frac{dF}{dt} = E\frac{dS}{dt}$$

If, however, the body is viscous, F will not remain constant, but will tend to disappear at a rate depending on the value of F and on the nature of the body. If we suppose this rate proportional to F, the equation may be written

$$\frac{dF}{dt} = E\frac{dS}{dt} - \frac{F}{T},$$

which will indicate the actual phenomena in an empirical manner. For if S be constant,

$$F = ESe^{-\frac{t}{T}},$$

shewing that F gradually disappears, so that if the body is left to itself it gradually loses any internal stress, and the pressures are finally distributed as in a fluid at rest.

If dS/dt is constant, that is, if there is a steady motion of the body which continually increases the displacement,

$$F = ET(dS/dt) + Ce^{-\frac{t}{T}}$$

shewing that F tends to a constant value depending on the rate of displacement. The quantity ET, by which the rate of displacement must be multiplied to get the force, may be called the coefficient of viscosity. It is the product of a coefficient of elasticity, E, and a time T, which may be called the 'time of relaxation' of the elastic force. In mobile fluids T is a very small fraction of a second, and E is not easily determined experimentally. In viscous solids T may be several hours or days, and then E is easily measured. It is possible that in some bodies T may be a function of F. . . ."

Twyman[5] stated that experiments showed that the rate at which the stress tends to disappear depends on the stress, as assumed by Maxwell; but he gave no evidence. Adams and Williamson,[9] in a study which laid the basis for the modern methods of annealing, found that the equations deduced by Maxwell did not fit the experimental facts. If the rate of release of strain were proportional to the amount of strain present, then the stress should decrease exponentially with time, and the experimental results should yield a straight line when log F is plotted against time. Such was not the case. Several other methods of plotting were

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[9] Adams, L. H., and Williamson, E. D., *J. Franklin Inst.*, **190**, 597 and 835 (1920).

tried, and it was found that the experimental results were fitted by the empirical formula

$$\frac{1}{\delta}-\frac{1}{\delta_0}=A't \qquad (1)$$

in which δ is the quantity actually measured, the birefringence of the path of length, l. The birefringence is related to the stress which produces it, F, by the equation $\delta = BFl$, in which the constant of proportionality, B, is the stress-optical coefficient, discussed on page 428.

Introducing stress units, (1) becomes

$$\frac{1}{F}-\frac{1}{F_0}=ABt, \qquad (2)$$

in which F_0 is the stress at the time $t = 0$, and $A = A'l$. Equation (2) is an integral of the differential equation

$$\frac{-dF}{dt}=ABF \qquad (3)$$

indicating that the rate of release of stress is proportional to the square of the stress, not to the first power, as assumed by Maxwell. The quantity A is the annealing constant, as defined by Adams and Williamson.

That equation (1) expresses the observed change of birefringence with time has been confirmed by several observers, including Hampton,[10] Morey,[11] and Lillie.[7] Lillie annealed a sample of glass at 453° for seven days. His measurements are well represented by the straight line in Fig. VI. 2.

Equation (1) was obtained empirically by Adams and Williamson as the best method of representing their experimental results, and as such it contains no assumptions. Preston[12] subsequently derived it by dimensional analysis on the assumption that the rate of release of stress is a function of the stress, F, and the viscosity, η. The differential equation obtained was

$$\frac{-dF}{dt}=\varphi(F,\eta)=C\frac{F^2}{\eta}$$

in which C is a dimensionless constant. If the rate of release of strain is a function also of one of the elastic constants, say, the modulus of rigidity, R, it follows that

$$\frac{-dF}{dt}=\frac{F^2}{\eta}\varphi\left(\frac{F}{R}\right)$$

It is difficult to give a physical interpretation of the unusual result that the rate of release of strain is dependent on the square of the stress.

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[10] Hampton, W. M., *Trans. Optical Soc. (London)*, **26**, 14 (1924-5); *J. Soc. Chem. Ind.*, **44B**, 207 (1925).

[11] Morey, G. W., and Warren, B. E., *Ind. Eng. Chem.*, **27**, 966 (1935).

[12] Preston, F. W., *Trans. Optical Soc. (London)*, **26**, 270 (1924-5); *Chemistry & Industry*, **45B**, 89 (1926).

Equation (1) gives an excellent representation of the experimental results at temperatures at which the stress is relieved in a few hours or days, but it does not necessarily follow that it can represent experiments made under other conditions. This was recognized by Adams and Williamson, who wrote: ". . . The fact was not disregarded that this is only an empirical equation, and like any other empirical equation is not to be relied upon for expressing the behavior of glass at temperatures far removed from those at which measurements were made. In order to determine the character of the agreement at much lower temperatures, a set of readings was taken with the light flint glass at about 300°, which is 85° below the lowest temperature at which the previous measurements were made. The glass anneals very slowly at this temperature, and after three weeks nearly half the original strain remained. Unfortunately, the curve representing the points where $1/\delta$ is plotted against t does not, in this case, prove to be a straight line, but is much curved at the beginning. We must conclude, therefore, that at the very low temperatures and for the initial part of the release of internal stress, formula * (1) fails to represent the relation between stress and time. Nevertheless, we believe that within the temperature range which is of

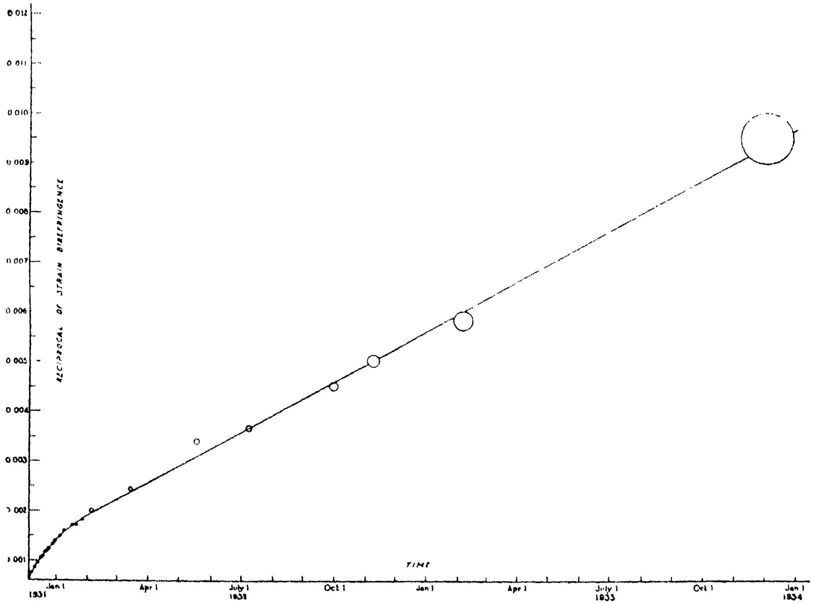

FIGURE VI. 1.—Annealing Curve, Reciprocal of Strain Birefringence against Time, of Pyrex Chemical Resistant Glass. After Morey and Warren.

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* Formula (7), in the notation of Adams and Williamson.

the greatest practical importance, and except for the first part of the stress to be relieved, the above-mentioned formula gives a useful and sufficiently accurate representation of the facts."

Morey[13] confirmed the above remarks in a study of the annealing of a sample of Pyrex chemical resistant glass at 430°, extending over a period of more than two years. The results obtained are shown in Fig. VI. 1. The initial curved part extended over a period of about six weeks, after which the change in birefringence with time is represented by the straight line, within experimental error.

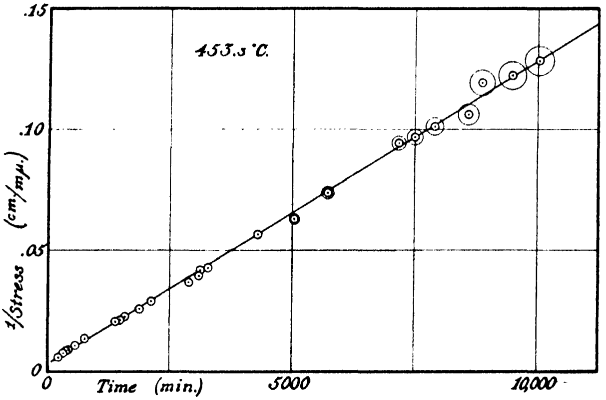

FIGURE VI. 2.—Annealing Curve, Reciprocal of Strain Birefringence against Time, of a Glass at 453° C. After Lillie.

Bailey and Sharp[14] studied the rate of release of stress under mechanical loading, as opposed to the release of the balanced system of internal stresses resulting from too rapid cooling, and found the Adams and Williamson formula to be in conflict with certain experiments. The release of mechanical stress became progressively slower with repeated loading, the bending stress always had a linear distribution, and no residual stress was observed on removing the load completely, all of which effects are in conflict with the conclusion that the rate of stress release is proportional to the square of the stress. They also found that the stress-optical coefficient did not change.

The difficulties enumerated above in the theory and application of the equation of Adams and Williamson, together with the fact that it gives the only satisfactory representation of the rate of release of strain under the experimental conditions for which it was derived, led Littleton[15] to suggest that there were two processes taking place simul-

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[13] Morey, G. W., and Warren, B. E., *Ind. Eng. Chem.*, **27**, 966, 968 (1935).

[14] Bailey, J., and Sharp, D. E., *J. Am. Ceram. Soc.*, **16**, 367 (1933).

[15] Littleton, J. T., *J. Am. Ceram. Soc.*, **17**, 43 (1934).

taneously; a release of strain and a change in viscosity, with a relationship between the two processes which would give an expression dimensionally correct, and in harmony with the square law. Lillie[16] had previously shown that in the annealing range the viscosity changes with time, at a rate decreasing with increasing viscosity; and that the same, and presumably equilibrium, viscosity would be reached irrespective of the thermal history of the sample. Littleton showed that when the ratio of the logarithm of the stress to the coeval viscosity is plotted against the rate of decrease of stress a straight line of unit slope is obtained. The equation of the curve obtained was: $-df/dt = 6.7 \times 10^{10} (f/\eta)$, and the constant necessarily has the dimensions of a modulus of elasticity.

Much of the difficulty of testing the validity of the various suggested relations between rate of release of stress and other properties has arisen from the measurements usually having been made by different people on different glasses of different thermal history. Lillie[7] made an adequate study which has removed these objections, and clarified the subject of the release of strain. He used an ordinary lime bulb-glass, and the samples were all taken from large slabs poured consecutively, and accordingly were as nearly identical in composition as possible. "Four types of measurements were made: (a) ordinary annealing runs on large slabs of glass previously chilled under known conditions; (b) viscosity-time determinations on fibers actually chilled under conditions similar to those of the slabs in (a); (c) stress-release runs on beams of annealed glass held in a constant configuration in a screw press; and (d) viscosity-time determinations on fibers annealed along with the beams in (c).

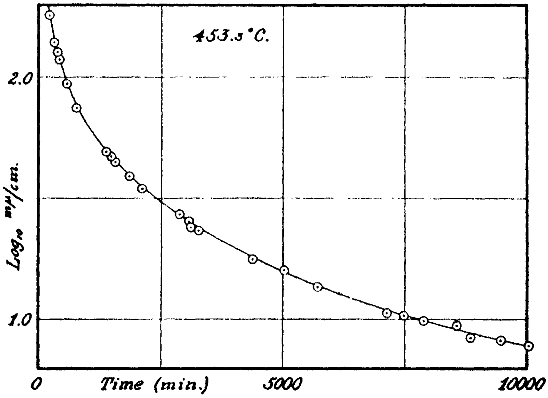

FIGURE VI. 3.—Annealing Curve, Logarithm of Strain Birefringence against Time, using the Same Data as in Fig. VI. 2. After Lillie.

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[16] Lillie, H. R., *J. Am. Ceram. Soc.*, **16**, 619 (1933) cf. pp. 162, 196.

All four individual experiments were carried out at two temperatures, 455° and 475°. The greatest care was taken to have all heat treatments exactly parallel in the (a), (b), (c), and (d) heat combinations, while temperatures throughout the extended runs were constant within a degree." The runs at the two temperatures led to the same conclusions, and only those at the lower temperature are reproduced.

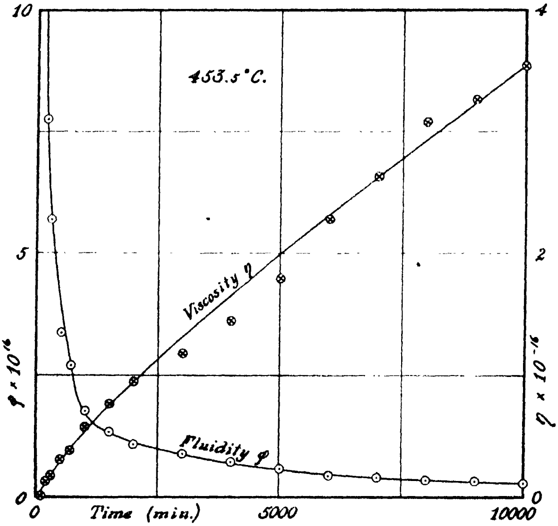

FIGURE VI. 4.—Viscosity-Time and Fluidity-Time Curves for a Chilled Fiber at 453° C. (This Figure is plotted incorrectly; the values should be respectively multiplied by, and divided by, 1.18 to give correct values.) After Lillie.

Fig. VI. 2 represents the release of strain plotted according to equation (1), and it affords an excellent verification of the method of plotting proposed by Adams and Williamson. The annealing constant, A, is 1.28×10^{-5}.

A relation between the rate of release of stress and viscosity which is dimensionally correct is

$$\frac{-dF}{dt} = \frac{MF}{\eta} = MF\varphi, \tag{4}$$

in which M is a constant having the dimensions of a modulus of elasticity. If the fluidity, φ, is assumed constant, the integral is

$$\log F_0 - \log F = M \varphi t,$$

a plot of which, using the same data as in Fig. VI. 2, is shown in Fig. VI. 3. From these two figures, "One would naturally assume that equation (1) expresses the true annealing law. But the viscosity varies widely during the time of the experiment; in fact [Fig. VI. 4] the variation is a 25-fold one, being from about 0.12 × 10^{16} to more than 3 × 10^{16} poises."

Equation (4) may be written

$$\frac{-d\log F}{dt} = M\varphi \tag{5}$$

a plot of which is shown in Fig. VI. 5. The values of $-(d\log F)/dt$ are taken from Fig. VI. 4, and the fluidity is that directly observed at the corresponding time. The curve is a straight line.

Experiments on the release of mechanical strain confirmed the observation of Bailey and Sharp that the annealing constant, A, decreases with repeated loading. Fig. VI. 6 shows the "Adams and Williamson" plot, in which A decreases from 7.75×10^{-6} at the beginning of the first loading to 1.2×10^{-6} in the last loading, which values are to be compared with 1.28×10^{-5}, obtained from Fig. VI. 2. If at a given treatment, the fluidity, φ, in equation (4) is a function of time only, then $-d(\log F)/dt$ is also a function of time, independent of F. Therefore, it should be possible to plot log F against total time and make a smooth curve, provided the proper amount is subtracted from the logarithms during the individual loadings, which has been done in Fig. VI. 7. "In order to be sure that the composite curve made up in this way is the same as one for a single loading, a check test was run extending to about 4200 minutes. The result agreed so well with Fig. VI. 7 that at no time

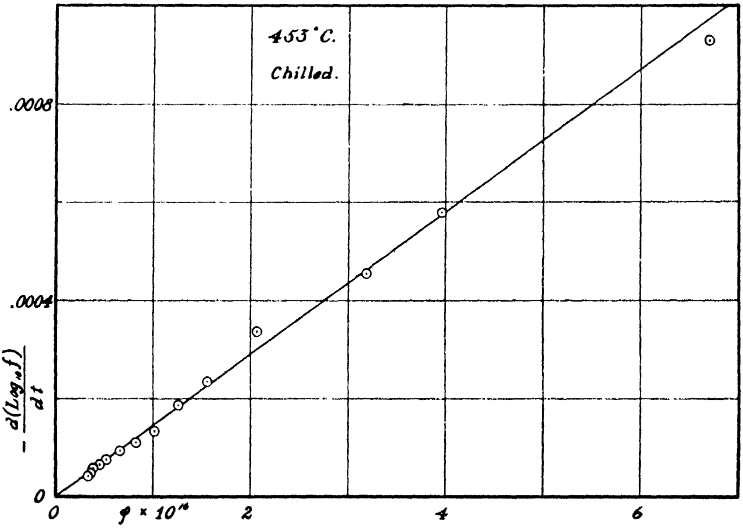

FIGURE VI. 5.—The Linear Relationship between Time Rate of Change of Stress and Fluidity, at 453° C. After Lillie.

did the slopes differ by so much as 5 per cent (which would correspond to about 0.6° difference). This check test also served to show that the anomalous high rate of stress release immediately following the application of each new load is an elastic reaction independent of any real viscous flow."

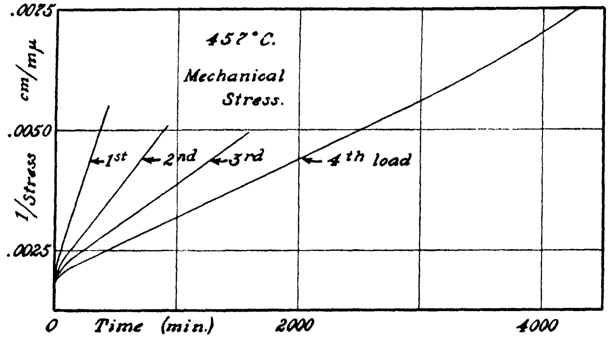

FIGURE VI. 6.—The Reciprocal of Strain Birefringence, plotted against Time, of Stress resulting from Repeated Mechanical Loading at 457° C. After Lillie.

In Fig. VI. 7 are plotted corresponding values for a glass "about 200° harder" than the one under discussion and for fused silica, and the curves indicate that the anomalous high rate of stress release is not caused by elasticity or creep in the apparatus. A plot of the results obtained under mechanical stress according to equation (5) is shown in Fig. VI. 8, and it also is a straight line.

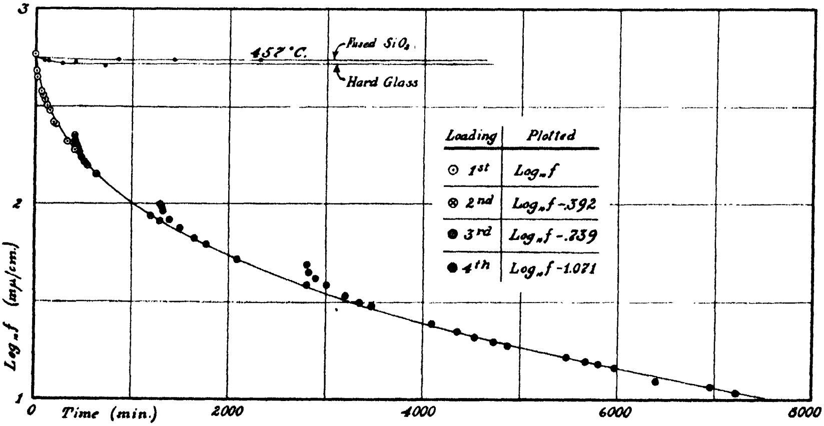

FIGURE VI. 7.—Logarithmic Plot of the Release of Stress resulting from Repeated Mechanical Loading at 457° C. After Lillie.

The constant M, which has the dimensions of a modulus of elasticity, is generally of the same order of magnitude in all the experiments. The results for release of thermal strain gave $M = 5.4 \times 10^{10}$ dynes per cm. at 453°, 5.7×10^{10} at 471°; and the results for release of mechanical strain gave 6.8×10^{10} and 5.6×10^{10}. The relation, if any, between M and the moduli of elasticity is not known. Young's modulus for this glass is 6.8×10^{11} dynes/cm.^{2}, Poisson's ratio, 0.24, which gives 2.74×10^{9} for the shear modulus, R. M accordingly is about one-fourth the shear modulus at room temperature, as was found by Littleton.

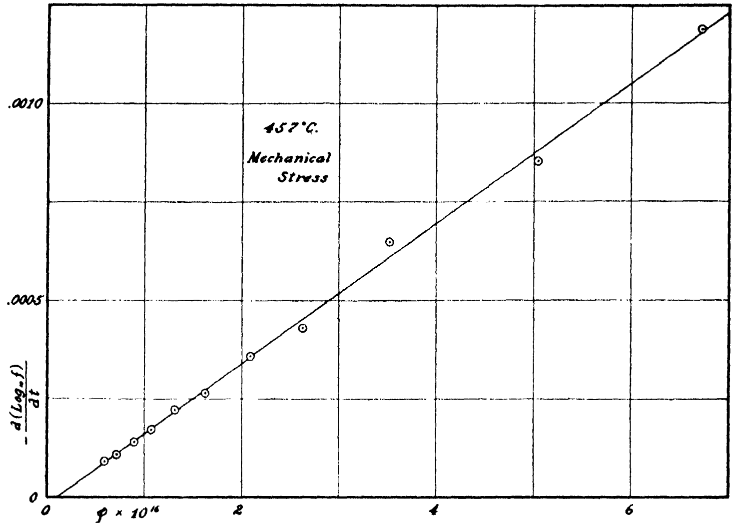

FIGURE VI. 8.—The Linear Relationship between dF/dt and $f\varphi$, for Release of Mechanical Stress at 457° C. After Lillie.

It may, accordingly, be taken as established that the release of strain in glass is determined by the viscosity; and that in the usual experiments the viscosity is changing at such a rate during the annealing as to cause the total effect to follow the time law discovered by Adams and Williamson and expressed in equation (1). An absolute correspondence to that law would require a predetermined rate of change of viscosity with time, which would not be true at more than one temperature; but the law is true for only a small temperature range. Within that range, which is the range of practical importance, the Adams and Williamson law for the rate of decrease of strain with time, equation (1), affords the most convenient and accurate method of treating the annealing of glass of the usual commercial shapes and sizes.

Table VI. 1—Annealing Constants and Temperatures of Some Glasses *

After Adams and Williamson, and Morey

No.	Type	M_1	M_2	Annealing Temp., (° C.)	Batch Composition of Glasses Studied by Adams and Williamson								
					SiO_2	B_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	PbO	Al_2O_3
1	516/620	0.030	18.68	599	67	12	9	8	..	4	..	..	..
2	523/590	0.029	17.35	573	73.1	..	14	1	12	..	..	..	..
3	573/420	0.033	15.92	461	54	..	6	5	..	..	..	35	..
4	574/570	0.032	20.10	606	47	4	3	5	..	29	11	..	1
5	606/440	0.028	16.28	556	46	..	3	4	..	15	8	24	..
6	608/570	0.038	24.95	638	40	6	..	..	..	43	8	..	3
7	616/370	0.038	18.34	464	45	..	3	4	..	..	..	48	..
8	655/330	0.037	17.51	454	42	..	3	3	..	..	..	52	..
9	756/270	0.033	15.03	434	28	..	..	3	..	..	..	69	..
10	511/631	0.031	18.83	587									
11	514/635	0.036	21.67	582									
12	563/500	0.036	20.44	549									
13	611/569	0.023	16.79	700									
14	617/570	0.035	23.77	659									

* Values of constants M_1 and M_2 in the equation $\log A = M_1\theta - M_2$, from which may be calculated the annealing constant, A. The annealing temperature is defined as that at which the strain will decrease from infinity to 2.5 mμ in two minutes, calculated from the formula $At = (1/\Delta n) - (1/\Delta n_0)$, in which Δn = birefringence in mμ, t = time in minutes. Compositions of glasses 1 to 9, by Adams and Williamson, are given above; those of glasses 10 to 16, by Morey, may be inferred from those of similar optical properties in Table III. 4.

The Annealing of Glass

Adams and Williamson based their treatment of the annealing of glass on their equation

$$\frac{1}{\delta}-\frac{1}{\delta_0}=A't, \tag{1}$$

in which δ is the observed birefringence of the path of length, l. It is sometimes more convenient to make use of the birefringence per cm. path, in which case the equation becomes

$$\frac{1}{(\Delta n)}-\frac{1}{(\Delta n)_0}=At,$$

in which Δn is the difference in refractive index in mμ of the fast and slow rays in the strained glass, $\delta = l\Delta n$, and $A = A'l$. If it is preferred to discuss the strain in terms of the stress, F, it will be remembered that $\Delta n = BF$, in which B is the stress-optical coefficient.

The annealing constant, A, determines the time necessary to anneal the glass at constant temperature. Adams and Williamson determined A for a number of glasses at a series of temperatures, and found, in agreement with the observations of Twyman,[5] that A is a simple exponential function of the temperature. Their results are represented by the formula

$$\log A = M_1\theta - M_2 \tag{6}$$

in which θ is temperature in °C., and M_1 and M_2 are experimental constants. The values of M_1 and M_2 for several glasses are in Table VI. 1, which also includes unpublished results of G. W. Morey on some additional glasses. The compositions of the glasses studied by Adams and Williamson are in Table VI. 1; the glasses studied by Morey were of conventional compositions which can be inferred from those of glasses in Table III. 4 having similar optical properties.

Both Adams and Williamson and Littleton and Roberts made it clear that the "annealing temperature" is not a uniquely determined temperature, but one which depends also on the annealing time, and neither variable can be specified without the other. Most definitions of the annealing temperature refer to a temperature at which the strain disappears quickly. Wright and Morey[17] used this temperature, which is readily recognizable in practice, in their study of the annealing of optical glass, and Turner and his co-workers used essentially the same definition. Adams and Williamson defined the "annealing temperature" as that at which the strain falls from 50 mμ to 2.5 mμ per cm. path in two minutes. In a later publication, Adams[18] pointed out that the time necessary for annealing is not greatly influenced by the initial stress, provided the initial stress is several times the final stress, and modified

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[17] Wright, F. E., "The Manufacture of Optical Glass and Optical Systems," 185, U. S. Ordnance Dept., Doc. No. 2037, Govt. Printing Office, Washington, 1921.

[18] Adams, L. H., *J. Franklin Inst.*, **216**, 39-71 (1933).

the definition of the annealing temperature by assuming the initial strain to be infinite. Then the annealing time, t_a, becomes the product of the annealing constant, A, and the prescribed final strain. Thus

$$t_a = \frac{l}{A(\Delta n)_a}$$

The precise formulation of the factors in the removal of strain enabled Adams and Williamson to discuss the practical problem in an exhaustive manner. Their detailed analysis of the temperature distribution in glass of various shapes cooled under different conditions, and of optical path differences caused by thermal gradients, is reproduced in Chapter XIV. Adams[18] condensed the earlier treatment of the calculation of annealing schedules as follows:

> ". . . The annealing of glass consists of two principal steps, first, the removal of the internal stress, and second, the prevention of its return upon subsequent cooling. The problem of annealing thus resolves itself into a quantitative delineation of these two factors. For the first, it is necessary to have available the data from which A, the annealing constant, can be determined at any temperature, and for the second it is necessary to formulate the relation between the permanent stress received and the conditions of cooling, by utilization of the principle stated above, *viz.*, that the permanent stress is numerically equal to that part of the temporary stress which is lost at the beginning of cooling. In terms of birefringence, Δn, the temporary stress in a material that is being heated or cooled at a constant rate, h, may be obtained from the equation,
>
> $$\Delta N = 10^7 \Delta n = ch. \qquad (7)$$
>
> Here, ΔN is the relative path difference in mμ per cm., and c is a constant for a given specimen but varies with the material and in general is proportional to the square of the size. For a slab or disk of optical crown glass or of plate glass, of thickness $2a$, viewed longitudinally along the middle, $c = 13a^2$ if a is expressed in centimeters, h in deg. C. per min., and ΔN in mμ per cm.* For Pyrex glass c is

* "The complete definition is as follows:

$$c = 10^7 \frac{\alpha B a^2}{6\kappa(\frac{1}{6}R + \frac{2}{9}K)},$$

in which α is the coefficient of linear expansion, B is the birefringence-stress ratio, κ is the thermal diffusity, R is the rigidity, and K is the bulk modulus.

"The values of c as given are intended to be only approximate but are calculated from the best data available in the literature. A calculation by Dr. G. V. McCauley (personal communication to the author), utilizing some unpublished data on the physical constants of Pyrex resistant glass, indicates that c for this material is about 25 per cent higher than the value given above."

equal to about $3a^2$ under the same conditions; and for silica glass c is equal to about $0.6a^2$ . . ."

Adopting a suggestion of G. V. McCauley that the temperature interval in which A doubles, denoted by p, be used in the calculations, instead of a rough average value of 10°, Adams revised the earlier procedure:

". . . The glass is held at a temperature θ_0, such that A has the value,

$$A_0 = \frac{1}{2pc}$$

for a time, in minutes,

$$a = \frac{4pc}{(\Delta n)_s}$$

and then cooled at a rate which initially is $(\Delta n_s)/c$ and which increases, as the temperature is lowered, according to the equation,

$$h = \frac{(\Delta n)_s}{2c}\left(1 + 2^{(\theta_0 - \theta)/2p}\right)$$

In actual practice little time is saved by continuing to increase the rate after it has become very high, and in any case the maximum cooling rate is limited to about $200/c$ (corresponding to a stress of about $\frac{1}{4}$ of the breaking strength), if danger of breakage, on account of high temporary stresses, is to be avoided. In practice more attention should be paid to the actual cooling-rate at various temperatures than to the time-temperature curve, but this curve may be evaluated directly from the integrated form of the preceding equation,

$$= \frac{4pc}{(\Delta n)_s}\left[\frac{\theta_0 - \theta}{2p} - \frac{\log\left(1 + 2^{(\theta_0 - \theta)/2p}\right)}{\log 2} + 1\right].$$

Since c varies as a^2 it is evident that the time required for annealing a piece of glass increases rapidly with the size of the article; increasing the thickness of a disk by a factor of 10 would increase the annealing time by a factor of 100 (and would require a lowering of the annealing temperature by about 65°).

"Circumstances may arise that make it inexpedient to carry out the annealing at exactly the optimum temperature, *i. e.*, at the temperature for which $A = \frac{1}{2}pc$. In that case, the annealing temperature θ' (or the corresponding A') is selected, and a value is chosen for $(\Delta n)_a$ (that part of $(\Delta n)_s$ which it is desired to leave in the glass just before the cooling begins, the remainder, $(\Delta n)_c$, being acquired during the cooling), whereupon the glass is held at θ' for the time,

$$t_a = \frac{1}{A'(\Delta n)_a}$$

and then cooled at the rate,

$$h = \frac{(\Delta n)_c}{2pc^2A'}(1 + 2^{(\theta' - \theta)/2p}).$$

In this more general case the cooling time is

$$t_c = \frac{4p^2c^2A'}{(\Delta n)_c}.$$

If we retain the condition that $(\Delta n)_a = (\Delta n)_c$ (but not necessarily that $t_a = t_c$) we find that a small change in θ, above or below θ_0, makes a considerable change in the total time required; a change of 10°, 20°, or 30° in either direction increases the time by the factor 1.25, 2.1, or 4.1, respectively.

"On the other hand, the most favorable value for $(\Delta n)_a$ for a given θ may be found by writing an expression for t, the sum of t_a and t_c, and setting $dt/d(\Delta n)_a$ equal to zero. In this way we find that for a predetermined temperature, the glass should be held at this temperature for a time such that $(\Delta n)_a$ will have the value,

$$(\Delta n)_a = \frac{(\Delta n)_s}{1 + 2pA'c}.$$

Annealing of Pyrex Chemical Resistant Glass

Morey [11] studied the annealing of Pyrex chemical resistant glass over an extended range of temperatures, and found equation (6) to be

$$\log A = 0.034\,\theta - 21.686$$

from which can be calculated the annealing time for any temperature. "But the practical problem includes not only the removal of strain at some annealing temperature but also the cooling of the ware without the introduction of further strain. This may be done by any one of a number of schedules in which the length of time the glass is held at constant temperature and the rate at which it is cooled are changed. For large pieces the most advantageous method of cooling is one at which half of the final allowable strain is allowed to enter during the cooling process, which is then carried out at a rate increasing with decreasing temperature, according to conditions determined by the dimensions of the piece."

"For most blown glassware in which the maximum thickness does not exceed 1 cm. and for laboratories in which equipment is not available to control the rate of cooling according to a prescribed schedule, the most satisfactory procedure is to anneal at a constant low temperature such that no strain will be introduced if the furnace is turned off and allowed to cool freely, or with a minimum of attention. If the glass is annealed for two hours at 550° C., the strain will be reduced to less than 10 mμ per cm. Then if it is cooled at an initial rate of 50° C. per minute, the amount of strain introduced during the cooling will not exceed 10 mμ, and the glass will be satisfactorily annealed. Few furnaces can cool more rapidly, and in general the initial rate of cooling will be less. The resulting maximum stress of 20 mμ per cm. is excellent annealing, corresponding to a stress in Pyrex chemical resistant glass of about 6 kg. per sq. cm., while its tensile strength is at least 700 kg. per sq. cm."

Other Studies of Annealing

An early study of annealing was that made by Schott,[19] who heated cylinders of glass 10 to 15 mm. in diameter and 20 to 40 mm. in length for 20 to 24 hours at various temperatures, and determined the number of rings visible between crossed nicols before and after the experiment. For the lowest temperature at which the number of rings could be observed to diminish he found the following values: Crown of the percentage composition: SiO_2, 66.90; B_2O_3, 2.50; Na_2O, 6.00; K_2O, 16.00; CaO, 5.10; PbO, 3.00; As_2O_5, 0.40; Mn_2O_3, 0.10, 400° to 410°; flint, near to (III. 4. 37), 350° to 360°; normal thermometer glass (III. 4. 61), 400° to 410°; and borosilicate thermometer glass 59^{III} (III. 4. 56), 430° to 440°.

A similar method was used by Grenet[20] and by Weidert and Berndt.[21] The latter authors slowly heated cubes of 25 mm. side, strained to a known degree, to a given temperature, and cooled them more slowly. The ratio between the final and the initial strain was found to be a minimum for a temperature dependent on the glass composition. Their results are given in Table V. 8.

The preceding methods for the determination of the annealing temperature have all been optical methods, based on the observation of the birefringence produced by strain. In addition, several other, more indirect, methods have been used.

Littleton and Roberts[22] determined the "annealing point" and the "strain point" by a method based on the rate of deformation under torsion at various temperatures and by comparison with a standard glass whose annealing time-temperature curve as measured by the optical method was known. The "annealing point" was defined as that temperature at which the glass annealed in 15 minutes; the "strain point" as the temperature of intersection of the temperature axis by the temperature-log fluidity (*i. e.*, rate of deformation) curve. Below this temperature there is practically no viscous yield; at it the glass anneals in about

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[19] Schott, O., *Z. Instrumentenk.*, **11**, 330 (1891).
[20] Grenet, L., in Le Chatelier, H., "Kieselsäure und Silicate"; p. 201, Leipzig, 1920.
[21] Weidert, F., and Berndt, G., *Z. tech. Physik*, **1**, 51 (1920).
[22] Littleton, J. T., and Roberts, E. H., *J. Optical Soc. Am.*, **4**, 224 (1920).

16 hours. Lillie[23] has determined the viscosity at the annealing point to be 2.5×10^{13} poises; at the strain point, 4×10^{14}. These results referred to fairly rapid heating, and in a later paper,[24] he gave the equilibrium viscosity at the annealing point as 4.7×10^{14} poises. The method was applied to various glasses made by the Corning Glass Works; the compositions were not given. For borosilicates, the annealing point ranged from 518° to 550° C., the strain point, from 470° to 503° C.; for lime glasses, 472° to 523° C., and 412° to 472° C.; for lead glasses, 419° to 451° C., and 353° to 382° C.

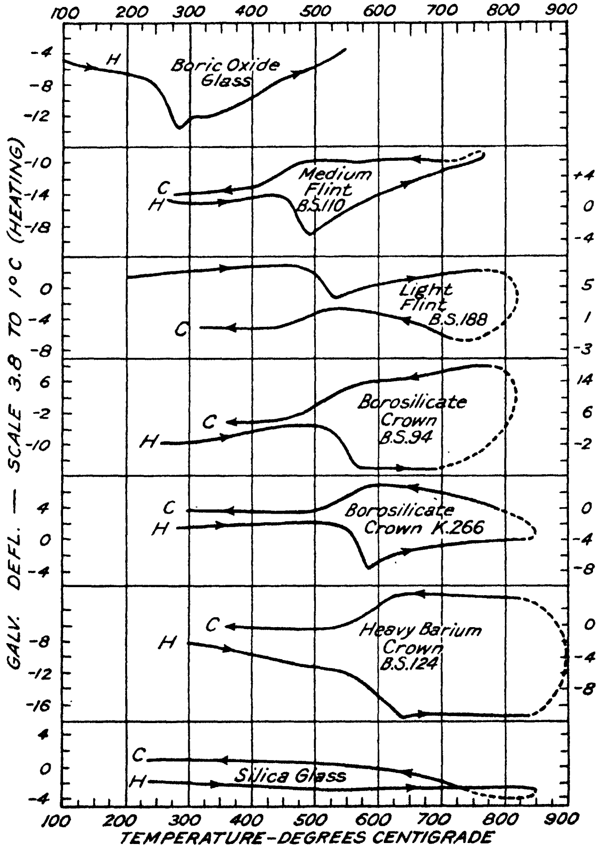

FIGURE VI. 9.—The Absorption and Evolution of Heat in Glass. After Tool and Valasek.

Tool and Valasek[25] compared the annealing temperatures obtained

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[23] Lillie, H. R., *J. Am. Ceram. Soc.*, **14**, 502 (1931).

[24] Lillie, H. R., *J. Am. Ceram. Soc.*, **16**, 619, 625 (1933).

[25] Tool, A. Q., and Valasek, J., *Bur. Standards Sci. Papers*, **358** (1920).

Table VI. 2A—Annealing Constants of Some Glasses of Compositions Indicated in Table VI. 2B

After Tool and Valasek

		Critical Ranges					
		Critical range				Annealing range, optical method	
		On cooling		On heating			
		A′	B′	A	B	Annealing temp.	Upper limit
No.	Name	$t \pm 15°$	$t \pm 10°$	$t \pm 10°$	$t \pm 5°$	$t \pm 15°$	$t \pm 15°$
1	Dense flint	435	495	460	490	...	...
2	Medium flint	405	480	455	485	460	510
3	Light flint	445	525	485	525	485	510
4	Barium flint	470	550	520	560	515	550
5	Light crown	450	525	495	525	480	530
6	Borosilicate crown ..	475	560	515	565	525	550
7	Borosilicate crown ..	500	585	545	585	525	550
8	Light barium crown..	520	590	575	605	570	610
9	Heavy barium crown	530	610	575	630	605	625
10	Pyrex chem. resist....			520	670		
11	Approx. B_2O_3			240	285		
12	0.13 Na_2O : 1 B_2O_3 ...			340	375		
13	0.28 Na_2O : 1 B_2O_3 ...			415	445		
14	0.44 Na_2O : 1 B_2O_3 ...			450	480		

by an optical method with those obtained from heating curves. In the optical method, cylinders of glass, placed between crossed nicols, were heated at a uniform rate, and the temperature at which the birefringence began to diminish was called the "annealing temperature," that at which it disappeared rapidly, the "upper limit." The thermal method consisted of heating the glass and a neutral body at a uniform rate, and of determining the temperature difference by a differential PtRh-Pt-PtRh ther-

Table VI. 2B—Compositions and Refractive Indices of Glasses Made at the National Bureau of Standards

After Williams and Rand

No.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	PbO	Sb_2O_3	As_2O_3	n_D	n_C	n_F	n_G
1-BS76	39.0		3.0	4.0	4.0			49.0	1.0	0.2	1.65555	1.65019	1.66922	1.68091
2-BS110	44.4		3.5	5.0	3.0			44.0		0.2	1.62495	1.62013	1.63701	1.64707
3-BS188	53.9		1.0	7.64	1.96			35.2		0.3	1.5805	1.5765	1.5903	
4-BS145	58.69	1.68	1.69	8.31		14.27	2.53	12.71		0.4	1.5521	1.5489	1.5597	1.56630
5-BS20	68.5	3.5	12.0	5.0		9.7	1.0			0.2	1.5179	1.5153	1.5328	1.5286
6-BS94	68.0	8.0	10.0	6.0		8.0	2.85			0.2	1.51977	1.51742	1.52584	1.53058
7-K266														
8-BS87	48.0	4.0	2.0	6.1		29.5	10.0			1.4	1.57340	1.57043	1.58057	1.58625
9-BS124	37.0	5.0		2.6		44.0	7.7	3.0		0.7	1.6199	1.61779	1.62939	1.63605

Table VI. 3—Annealing Temperatures of Some Glasses* Studied at the Department of Glass Technology, University of Sheffield, Sheffield, England

No.	Annealing Temp. (° C.)	No.	Annealing Temp. (° C.)	No.	Annealing Temp. (° C.)
1	490	443D	501	458	561
10	581	444B	510	459	560
441A	491	445D	522	460	562
442	492	446C	525		

* Compositions are in Table X. 3.

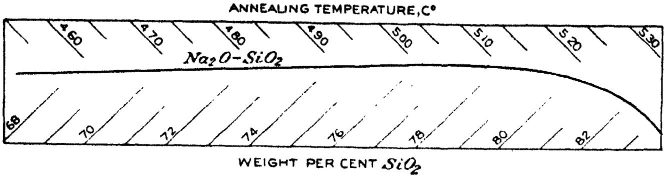

FIGURE VI. 10.—Annealing Temperatures of Glasses in the System Na_2O-SiO_2. After English, Hodkin, Muirhead and Turner.

mocouple. An absorption of heat was observed on heating, and an evolution of heat on cooling; the temperatures of the beginning (*A*) and the maximum (*B*) of the heat absorption, and the maximum (*B*′) and the end (*A*′) of the heat evolution, shown in Fig. VI. 9, were determined from the thermocouple reading. The various results for both methods are summarized in Table VI. 2. Glasses 1 to 9 were optical glasses made at the National Bureau of Standards, of the composition and optical properties given in Table VI. 2b, taken from Williams and Rand.[26]

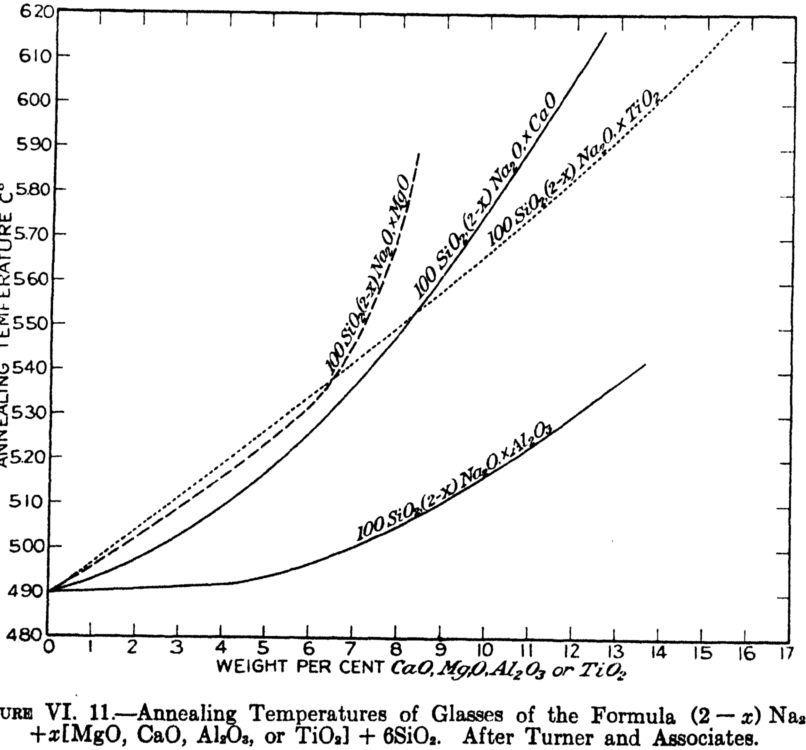

FIGURE VI. 11.—Annealing Temperatures of Glasses of the Formula $(2-x)$ Na_2O $+x$[MgO, CaO, Al_2O_3, or TiO_2] + $6SiO_2$. After Turner and Associates.

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[26] Williams, W. S., and Rand, C. C., *J. Am. Ceram. Soc.*, **2**, 422 (1919).

Glass 10 was Pyrex chemical resistant glass (composition III. 3. 20); and glasses 11 to 14 were of the composition given.

The preceding experimental work has been concerned mainly with the determination of the annealing temperature of commercial multicomponent glasses. An extensive series of experiments on the effect of change in annealing temperature with composition has been made by Turner and his co-workers at the Department of Glass Technology at the University of Sheffield. The annealing temperature adopted by them was that at which the birefringence due to strain disappeared "rapidly" when the glass was held at constant temperature; values so determined are included in Table VI. 3. The results of these experiments are shown by Figs. VI. 10, VI. 11, VI. 12, and V. 15.

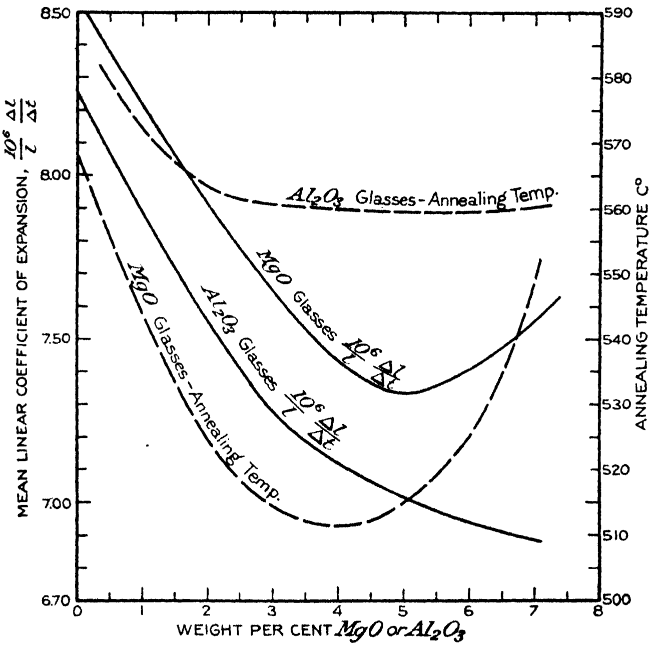

FIGURE VI. 12.—Annealing Temperatures and Thermal Expansions of Glasses of Compositions Derived from $1.2Na_2O + 0.8CaO + 6SiO_2$ by Substitution of MgO for CaO; and from $1.1Na_2O + 0.9CaO + 6SiO_2$ by Substitution of Al_2O_3 for CaO. After Turner and Associates.

Gehlhoff and Thomas[27] also determined the change in annealing temperature with composition in several series of glasses. The annealing temperature was that at which the strain disappeared "quickly" at a heating rate of 5° per minute. The effect of Na_2O or K_2O in the

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[27] Gehlhoff, G., and Thomas, M., *Z. tech. Physik*, **6**, 333 (1925).

binary M_2O-SiO_2 glasses is shown in Fig. VI. 13a. In the glass 0.18 Na_2O, 0.82 SiO_2 the effect of displacement of SiO_2 by CaO, BaO, or PbO is shown in Fig. VI. 13b; by B_2O_3, Al_2O_3, and Fe_2O_3 in Fig. VI. 13c; and by ZnO in Fig. VI. 13d. The results are in harmony with those of previous observers.

Sharp, Bailey, and Hyman [28] devised an apparatus which was similar to that used by Adams and Williamson for studying the rate of release of strain, but which was provided with a means of straining the glass by an applied load. In general the curves of stress release followed the Adams and Williamson rule, but some discrepancies led to a more intensive study by Bailey and Sharp.[29] In this study it was shown that the initial release of mechanical stress was more rapid than that required by the Adams and Williamson equation, but the final release was slower. Repeated loadings at the same temperature gave different values for the annealing constant, which is dependent on the thermal history of the glass. These experiments, and similar ones by Lillie, have already been discussed.

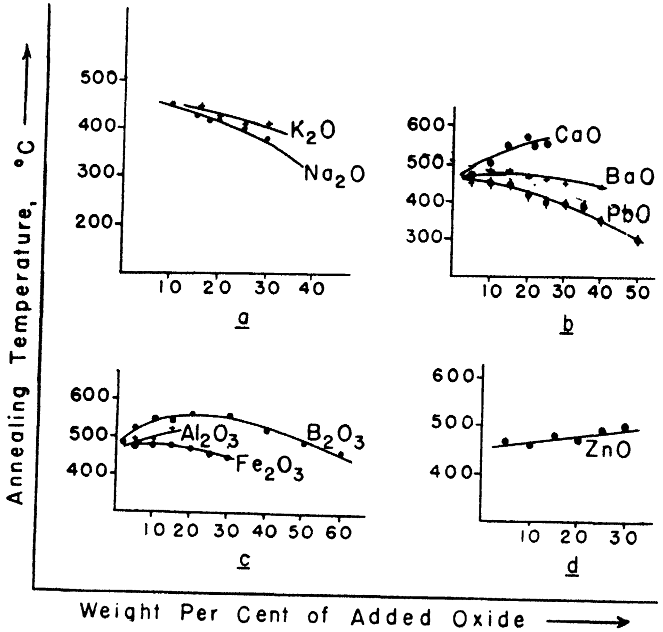

FIGURE VI. 13.—Change in Annealing Temperatures with Composition. After Gehlhoff and Thomas.

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[28] Sharp, D. E., Bailey, J., and Hyman, I., *J. Am. Ceram. Soc.*, **14**, 820 (1931).

[29] Bailey, J., and Sharp, D. E., *J. Am. Ceram. Soc.*, **16**, 367 (1933). Cf. p. 183.

Chapter VII

The Surface Tension of Glass

The surface of separation between any two phases possesses properties differing from those of matter in bulk, the difference manifesting itself in energy content in systems of one component, and in both energy content and composition in systems of more than one component. The general relation between energy of the surface ϵ^s, temperature T, entropy η, and the chemical potentials $\mu_1 \ldots . \mu_n$ of the masses $m_1 \ldots . m_n$ of which a phase is composed, is given by the equation[1]

$$d\epsilon^s = td\eta + \gamma ds + \mu_1 dm_1 + \ldots + \mu_n dm_n$$

in which s is the surface and γ a quantity called surface tension, defined by

$$\gamma = \frac{\delta\epsilon}{\delta s}$$

and the value of which is dependent on the nature and the state of the contiguous masses. Thus the surface tension refers to an interface between two phases. When the term is used without qualification, the adjoining phase is usually air, saturated with the vapor of the substance. The effect of surface tension in a one-component system is to decrease the area of the interface to a minimum consistent with other requirements; in a system of more than one component there is also a concentration at the interface of those components which reduce the surface tension. This concentration at the interface necessitates the diffusion of material both to and away from the interface, a process which is not instantaneous. Hence, in a multicomponent system there may be found two different limiting values for the surface tension, namely, a dynamic and a static. The dynamic surface tension refers to the instantaneous value given by a freshly formed surface, and is always higher than the static surface tension, which refers to the value attained when the interface has reached its equilibrium composition. The difference between the dynamic and static surface tensions in glasses is unknown, as is also the time required for the equilibrium value to be attained. Hiss[2] found that for a 0.284 molar solution of amyl alcohol in water, the dynamic value is 54.9, the static value is 34.8, and in 0.0189 second the value of 36.6 was obtained. In such cases the equilibrium is evidently attained

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[1] "The Scientific Papers of J. Willard Gibbs," eq. 501, Longmans, Green, New York, 1906.

[2] Freundlich, H., "Colloid and Capillary Chemistry," 52, translated from the 3rd German edition by H. S. Hatfield, Dutton, New York.

with great rapidity; but that such can be the case with glass is not probable.

It is probable that the attaining of the equilibrium surface tension requires not only a migration to the surface of some of the components, but also their orientation in the surface. The work of several investigators, notably Langmuir and Harkins, has shown that orientation of the surface molecules is probably the general rule, and the tendency may be pronounced in glass. Even at high temperature, however, the time required may be longer than afforded by the usual method of measurement.

The "surface tension" of glass refers to the interface between liquid and vapor or air. When glass meets a solid surface (for example, that of a refractory or a metal), three independent surface tensions, corresponding to the three interfaces liquid-air, solid-air, and solid-liquid, determine whether or not the liquid "wets" the solid, and whether or not it is able to penetrate the pores of the refractory. In the general case, the liquid meets the solid with formation of the angle of contact a, and equilibrium requires that

$$\sigma_{sl} = \sigma_{sg} + \sigma_{lg} \cos a$$

in which the subscripts s, l, and g refer to solid, liquid and gas. The difference between the interfacial tensions of the solid is called the adhesion tension j, given by

$$j = \sigma_{sl} - \sigma_{sg} = \sigma_{lg} \cos a.$$

In general the numerical values of the surface tensions at the solid interfaces cannot be measured, but important qualitative relations exist.

If wetting does not take place, the adhesion tension may be any fraction (positive or negative) of the surface tension of the liquid. If the liquid spreads out over the surface of the solid, that is, if the liquid completely wets the solid, the adhesion tension is equal to or greater than the surface tension of the liquid:

$$\sigma_{sg} > \sigma_{sl} + \sigma_{lg} \text{ or } \sigma_{sg} - \sigma_{sl} = j > \sigma_{lg}.$$

The possibility also exists that the surface is unwettable:

$$\sigma_{sl} > \sigma_{sg} + \sigma_{lg} \text{ or } (\sigma_{sg} - \sigma_{sl}) = -j > \sigma_{lg}.$$

In this case the interface solid-liquid is not formed.

Washburn[8] discussed the rate of penetration of a liquid into a cylindrical capillary tube, and derived the equation

$$x^2 = \frac{\sigma \cos \theta}{2\eta} rt$$

for the distance x penetrated in time t, by a liquid of viscosity η in

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[8] Washburn, E. W., *Phys. Rev.*, **17**, 273 (1921).

a capillary of radius r. The function $\frac{\sigma \cos \theta}{2\eta}$ is called "the coefficient of penetrance" or "the penetrability" of the liquid.

Units and Conversion Factors

The surface tension, a force per unit of length, and the surface energy, energy per unit of surface, have the same dimensions, MT^{-2}, and the numerical value of each is the same. When measured in mg. per mm., the conversion factor to dynes per centimeter is 9.80665; when in pounds per in., 1.7513×10^5. "The molar free surface energy is the product of the surface tension and that surface which is developed by a molar amount (determined say from the vapor density) of the liquid considered as a sphere."[4] If M is the molecular weight, v the specific volume, the molar free surface energy is $\sigma(Mv)^{\frac{2}{3}}$. This quantity, and especially its temperature coefficient, has been widely applied to the determination of the molecular weight of liquids. The method, however, has been discredited,[5] and the value to be used for the molecular weight of a glass is so uncertain, that an attempt to apply the rule of Eötvos, Ramsay, and Young to glasses is not worth while.

Experimental Results

The equilibrium shape assumed by a liquid at rest, as well as the forms assumed by a liquid in motion, are determined chiefly by the surface tension;[6] and each of these processes affords a possible method of measurement of surface tension. Few of the possible methods have been applied to glass, chiefly because of the experimental difficulties caused by the necessary high temperatures and high viscosity, and none of those applied has been wholly free from objection. The most common method for the measurement of the surface tension of aqueous solutions is that based on the rise of liquid in tubes of small bore, a method which obviously cannot be applied to glass.

In all the usual methods there is a balance between surface tension and opposing forces affecting the surface, and of these forces gravity most frequently is dominant. The density of the liquid at the temperature of the experiment becomes an important factor,* concerning which too little is known.

The simple technique of the drop weight method has led to its use by several investigators, but the results obtained are not satisfactory.

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[4] Freundlich, H., "Colloid and Capillary Chemistry," 31.

[5] Jaeger, F. M., *Proc. Acad. Sci. Amsterdam*, **17**, 416 (1914); *ibid.*, **19**, 396 (1916). Adam, N. K., *Phil. Mag.*, [7], **8**, 539 (1929).

[6] Dorsey, N. E., *Sci. Papers Bur. Standards*, **21**, 563 (1926) (Sci. Paper 540). This paper contains an excellent discussion of the methods of measuring surface tension.

* Cf. the discussion of the determination of density at high temperatures, on p. 259.

The conditions attending the breaking away of a drop of liquid are complex even as applied at ordinary temperatures, when selected tips are used for the flow of liquid; and the relation between drop weight and surface tension is still less simple when the drops are formed by heating in a flame the end of a glass rod. This was the method originally used by Quincke,[7] who gave 176.5 dynes per cm. at 1100° for a glass of unknown composition.

Tillotson [8] determined by a modified drop weight method at unknown temperatures the surface tensions of a number of experimental glasses. Within the limit of error of the method, his results agreed with Quincke's empirical relation:

$$W = \alpha d + \beta d^2$$

in which W is the drop weight, d the diameter of the fiber, α a factor dependent on surface tension, and β a factor which is dependent on the cohesion of the molten glass and which has the approximately constant value of 15. The surface tension ranged from 133 to 172 dynes per cm. for silicate glasses, to as low as 59 for Na_2O-B_2O_3 glass. It was found to be roughly a linear function of the composition; and the experimental results could be calculated from the formula

$$\gamma = a_1p_1 + a_2p_2 + a_3p_3 + \text{etc.},$$

in which p_1, p_2, p_3 are the percentages of the various oxides, and a_1, a_2, a_3 the following empirical factors for the respective oxides: BaO, 195; B_2O_3, 45; CaO, 323; Na_2O, 160; SiO_2, 129. As was stated by Tillotson, the method is of value chiefly in obtaining rapidly and easily comparable values of surface tensions rather than absolute values.

Lecrenier [9] and Lecrenier and Gilard [10] used the drop weight method, in which the drops were formed by issuing from a circular orifice (radius r = 1.928 mm.) in the bottom of the tubular platinum crucible in which the glass was heated. The surface tension was calculated by the formula of Guglielmo,[11]

$$\gamma = \frac{p}{2\pi r}\left(1 + \frac{r}{R}\right),$$

in which p = the weight of the globule in mg., and R the radius of curvature at the widest point of the globule. Measurements were made on two commercial glasses of unknown composition, a soda-lime glass and a crystal glass, with results shown in Table VII. 1. A.

The surface tensions of a number of experimental glasses determined in the same manner are given in Table VII. 1. B. Generalizations as to

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[7] Quincke, G., *Ann. Physik*, **134**, 356 (1868); **135**, 621 (1868).

[8] Tillotson, E. W., *Ind. Eng. Chem.*, **3**, 631 (1911); **4**, 651 (1912).

[9] Lecrenier, A., *Bull. Soc. Chim. Belg.*, **33**, 119 (1924).

[10] Lecrenier, A., and Gilard, P., *ibid.*, **34**, 27 (1925).

[11] Guglielmo, G., *Rend. Accad. Lincei* 12, 617 (1903).

TABLE VII. 1—The Surface Tension Results of Lecrenier

A. Commercial Glasses

Temperature (° C.)	Soda-lime glass (dynes/cm.)	Crystal glass (dynes/cm.)
1025	407.8	388.9
1125	406.2	384.0
1225	404.3	382.2

B. Experimental Glasses

Composition	Temp. (° C.)	
	1050°	1150°
$Na_2O \cdot CaO \cdot 6SiO_2$	473.7	471.0
$K_2O \cdot CaO \cdot 6SiO_2$	436.1	419.5
$\frac{1}{2}K_2O \cdot \frac{1}{2}Na_2O \cdot CaO \cdot 6SiO_2$	464.6	448.7
$Na_2O \cdot 0.5CaO \cdot 0.5MgO \cdot 6SiO_2$	476.7	472.3
$K_2O \cdot 0.5CaO \cdot 0.5MgO \cdot 6SiO_2$	463.3	448.1
$0.5Na_2O \cdot 5K_2O \cdot 0.5CaO \cdot 0.5MgO \cdot 6SiO_2$	473.0	471.6
$Na_2O \cdot 0.5CaO \cdot 0.5Al_2O_3 \cdot 6SiO_2$	508.0	497.2
$Na_2O \cdot 0.5CaO \cdot 0.5BaO \cdot 6SiO_2$	477.2	474.3
$K_2O \cdot 0.5CaO \cdot 0.5BaO \cdot 6SiO_2$	437.4	425.3
$Na_2O \cdot 0.8MgO \cdot 6SiO_2$	....	453.6
$Na_2O \cdot MgO \cdot 6SiO_2$	475.2	472.1
$Na_2O \cdot 1.2MgO \cdot 6SiO_2$	484.6	480.4
$1.2Na_2O \cdot 0.8CaO \cdot 6SiO_2$	466.4	....
$1.4Na_2O \cdot 0.6CaO \cdot 6SiO_2$	458.8	....
$1.6Na_2O \cdot 0.4CaO \cdot 6SiO_2$	449.5	....
$1.8Na_2O \cdot 0.2CaO \cdot 6SiO_2$	442.9	....
$Na_2O \cdot CaO \cdot 5SiO_2$	449.2	446.5
$Na_2O \cdot CaO \cdot B_2O_3 \cdot 5SiO_2$	441.6	437.2
$Na_2O \cdot 0.8CaO \cdot 6SiO_2$	....	452.9
$Na_2O \cdot 1.2CaO \cdot 6SiO_2$	480.1	476.2
$1.2Na_2O \cdot CaO \cdot 6SiO_2$	469.1	460.4
$0.8Na_2O \cdot CaO \cdot 6SiO_2$	....	478.9
$2Na_2O \cdot 6SiO_2$	433.5	....
$Na_2O \cdot CaO \cdot 6SiO_2 + 2\% Na_2SO_4$	468.0	462.6

the relation between surface tension and composition based on these results are to be accepted with caution.

Tammann[12] proposed a method for the determination of surface tension in the viscosity range from 10^4–10^6 poises, based on the shrinkage of a glass fiber of given proportions. When such a fiber is heated, its length at first increases, then decreases until the gravitational pull of the fiber becomes equal to the surface tension, after which the fiber again lengthens. The enlargement in diameter caused by shrinkage in length is a maximum just before the second elongation begins. The surface tension is calculated from the relation

$$2\gamma = \frac{\text{weight}}{\text{circumference}},$$

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[12] Tammann, G., and Rabe, H., *Z. anorg. allgem. Chem.*, **162**, 17 (1927); Tammann, G., and Tampke, R., *ibid.*, **162**, 1 (1927).

in which the weight taken is from the heated portion to the end of the thread. The first measurements, made on Thuringian glass and salicin, gave a positive temperature coefficient, said to be caused by the influence of moisture. The next measurements were made in dry air on salicin, piperine, and Jena Geräte II glass, and showed the normal temperature coefficient. The results for the Geräte glass are given in Table VII. 2; d is the diameter of the unheated portion of the thread, t_1 the temperature at which the thread began to shrink, and t_2 that at which it began to lengthen.

TABLE VII. 2—The Surface Tension of Jena Geräte Glass

After Tammann

Diameter (mm.)	t_1	t_2	Surface tension (dynes/cm.)
0.101	444	547	168.3
0.065	455	552	167.4
0.243	457	560	166.7
0.160	482	592	165.0

Keppeler[13] used a similar method, with fibers of circular cross-section, 0.4 mm. in diameter. By means of a small flame a position was found at which the glass neither thickened nor elongated, and the length of the fiber below this position was measured. The surface tensions of two Thuringian glasses (composition not given) were 136 and 151, and of a B_2O_3-glass, 32.7 dynes per cm. Measurements by the fiber method are included with those made on the same glasses by the bubble method in Table VII. 7.

Griffith[14] determined the surface tension of a glass of the composition SiO_2, 69.2; K_2O, 12.0; Na_2O, 0.9; Al_2O_3, 11.8; CaO, 4.5; MnO, 0.9 at 1110° by the method of sessile drops, and from 730° to 900° by the measurement of the sag in horizontal glass fibers loaded at their middle points. Details are not given. The decidedly irregular results, given in Table VII. 3, were extrapolated to 16°, but the value of "surface tension" so obtained probably is of little significance. This method could not be used above 900°, because the viscosity was insufficient to enable an observation to be made before the fibers commenced to break up into globules. Below 730°, observations made on fibers of different diameters were inconsistent, the apparent surface tension being higher

TABLE VII. 3—Surface Tension of a Glass

After Griffith

Temperature (° C.)	1110	905	896	852	833	820	801	760	745
Surface Tension (dynes/cm.)	403	419	438	437	445	437	451	447	440

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[13] Keppeler, G., *J. Soc. Glass Tech.*, **21**, 53 (1937).

[14] Griffith, A. A., *Trans. Roy. Soc. (London)*, **A**, **221**, 163 (1920).

for the larger fibers, from which it was inferred that the glass used was not a perfectly viscous liquid. "The maximum tension (apart from surface tension) which could be permanently sustained was zero at 730° C., 1.3 lb. per sq. in. at 657° C., and 24 lb. per sq. in. at 540° C. At lower temperatures the rates of increase both of this 'solid stress' and of the viscosity were enormously greater." These results are in conflict with measurements of viscosity by the fiber elongation method in the same temperature range.

The shape assumed by a sessile drop affords a method for the determination[15] of surface tension, first applied to glass by Quincke,[16] who obtained a value of 84.7 dynes per cm. for B_2O_3 at 1700°. Taylor and Ellefson[17] measured the dimensions of the drop at high temperatures by means of a telescope with special eye-piece, and also photographed the sessile drop. They found that the shape of the drop and the contact angle on platinum was affected by oxygen in the surrounding atmosphere, but the contact angle on gold was not affected. One to two hours were required for the drop to assume its final shape.

TABLE VII. 4—Surface Tension of Li_2SiO_3

After Jaeger

Temperature (° C.)	1254	1380	1421	1479	1550	1601
Surface tension (dynes/cm.)	374.6	358.2	356.2	352.8	348.7	346.6

A bubble blown on the end of a vertical tube dipping into a liquid will have the form of a segment of a sphere if the radius of the tube is small. As the bubble is blown the radius of the sphere first will decrease until the bubble becomes hemispherical, then it will increase. When the bubble is a hemisphere the radius is that of the tube, and a minimum; the corresponding pressure is a maximum. From the dimensions of the bubble and tube, and the density of the glass, the surface tension can be calculated. This bubble pressure method was developed by Jaeger,[18] who studied molten lithium metasilicate, Li_2SiO_3, with the results[19] given in Table VII. 4. Jaeger stated[20] that viscosity prevented determination of surface tension "only, when the viscosity reached such enormous magnitude that the liquid became glassy or gelatinous, and did not, or hardly, move on reversing the vessel."

The bubble pressure method has been used also by Parmelee and

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[15] Dorsey, N. E., *Sci. Papers Bur. Standards*, **21**, 563 (1926) (Sci. Paper 540). Bashforth, F., and Adams, J. C., "An Attempt to Test the Theories of Capillary Action," Cambridge Univ. Press, 1883.

[16] Quincke, G., *Ann. Physik*, **138**, 141 (1869).

[17] Ellefson, B. S., and Taylor, N. W., *J. Am. Ceram. Soc.*, **21**, 193, 205 (1938).

[18] Jaeger, F. M., Numerous papers in *Proc. Acad. Sci. Amsterdam* from 1914 to 1917, summarized in *Z. anorg. allgem. Chem.*, **101**, 1 (1917).

[19] Jaeger, F. M., *Proc. Acad. Sci. Amsterdam*, **17**, 364 (1914).

[20] Jaeger, F. M., *ibid.*, **17**, 425 (1914).

his associates. Parmelee and Lyon[21] measured the surface tension of a melt of the composition: SiO_2, 64.86%; B_2O_3, 12.96%; Na_2O, 18.56%; R_2O_3, 1.56% from 1050° to 1350°, with the results shown in Fig. VII. 1.

Parmelee and Harman[22] studied the effect on the surface tension of a glass of the addition of 2, 4, and 8 parts of alumina, Al_2O_3, to 100 parts of the glass, with the results shown in Fig. VII. 2. The glasses, which were not analyzed, had the batch composition: SiO_2, 73.18%; Na_2O, 16.02%; CaO, 7.77%; MgO, 3.02%.

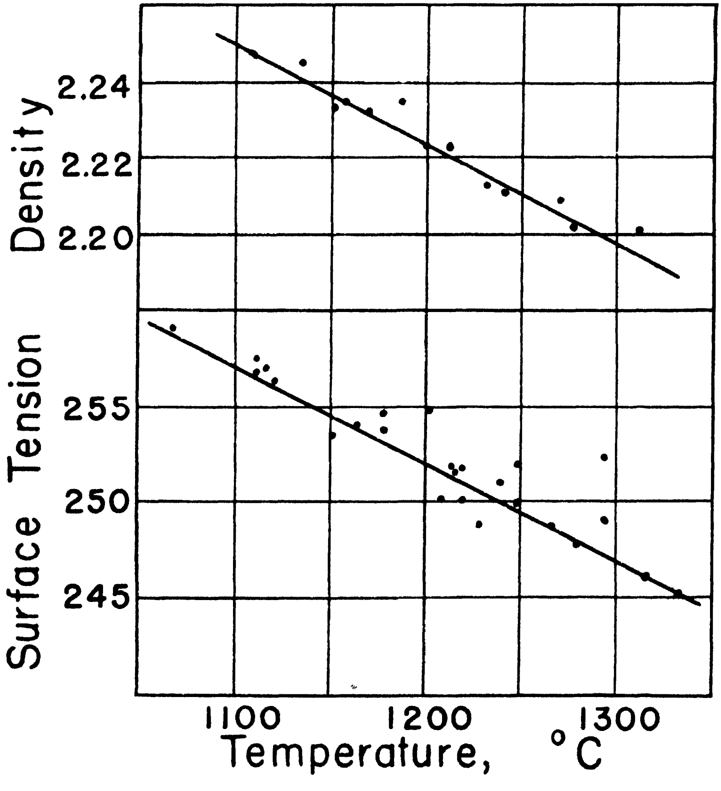

FIGURE VII. 1. Surface Tension in Dynes per Cm. of a Melt of Composition given in Text. After Parmelee and Lyon.

Badger, Parmelee, and Williams[23] used a base glass, of molecular composition $1.4\,Na_2O + 0.9\,CaO + 6.0\,SiO_2$ (SiO_2, 72.5%; Na_2O, 17.4%; CaO, 10.1%) to which was added the amounts of other oxides indicated

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[21] Parmelee, C. W., and Lyon, K. C., *J. Soc. Glass Tech.*, **21**, **44** (1937).

[22] Parmelee, C. W., and Harman, C. G., *J. Am. Ceram. Soc.*, **20**, **224** (1937).

[23] Badger, A. E., Parmelee, C. W., and Williams, A. E., *J. Am. Ceram. Soc.*, **20**, **325** (1937).

in Table VII. 5. Surface tensions were measured at 1200° C. and at 1350° C. by two observers. The maximum difference between a single determination and the average ranged from 0.2 to 6.9 (number of observers not given); the difference between the values obtained by the two observers ranged from 0.1 to 10.4, with an average difference of 3.8.

Badger, Parmelee, and Williams also measured the surface tension for some analyzed commercial glasses, with the results given in Table VII. 6, together with the compositions of the glasses. For a soft-coat enamel, of batch composition: SiO_2, 40.9; B_2O_3, 17.5; Na_2O, 4.5; K_2O, 15.3; CaO, 8.4; Al_2O_3, 7.7; Fe_2O_3, trace; MnO_2, 1.2; NiO, 0.5; CaO, 0.6; F_2, 3.5, the value of 244 dynes per cm. was found at 925°. The glass was obtained from W. N. Harrison of the National Bureau of Standards, who obtained 245.8 dynes per cm. at 925°, using a dipping cylinder method.

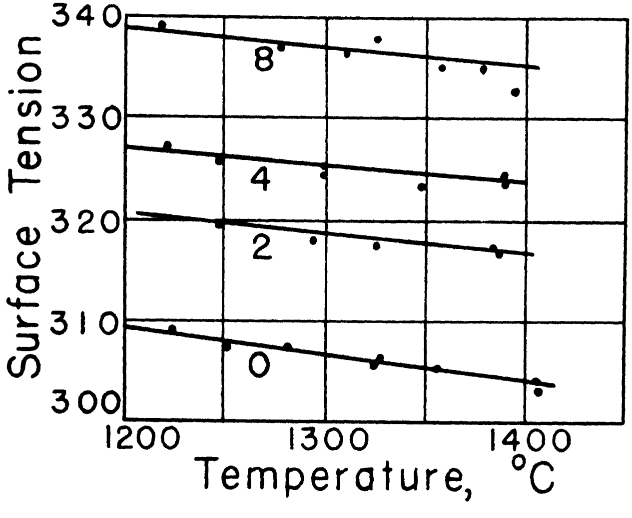

FIGURE VII. 2.—Change in Surface Tension in Dynes per Cm. with Temperature of a Series of Melts Containing the Percentages of Alumina indicated on the Curves. After Parmelee and Harman.

Keppeler[24] also used the bubble method to measure the surface tension of the glasses of the batch composition given in Table VII. 7. The deviation of the actual composition from that calculated is shown by the following analytical values: I, SiO_2, 75.8; II, SiO_2, 74.41; B_2O_3, 1.49; III, SiO_2, 72.75; B_2O_3, 2.99; IV, SiO_2, 72.53; B_2O_3, 3.75; V, SiO_2, 68.51; B_2O_3, 7.10; VI, SiO_2, 66.00; B_2O_3, 9.05. Table VII. 7 gives the results from both the fiber elongation method and the bubble method;

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[24] Keppeler, G., *J. Soc. Glass Tech.*, 21, 53 (1937).

TABLE VII. 5—Effect of Miscellaneous Added Oxides on the Surface Tension of a Glass of the Molecular Composition: $1.4Na_2O + 0.9CaO + 6SiO_2$

After Badger, Parmelee and Williams

Added Oxide	Amount Added (Moles)	Surface tension (dynes/cm.) 1200°	Surface tension (dynes/cm.) 1350°
None		304	302
Li_2O	0.015	306	305
Na_2O	0.015	300	298
K_2O	0.015	292	286
MgO	0.030	316	314
CaO	0.030	312	310
BaO	0.030	312	311
ZnO	0.030	315	312
B_2O_3	0.015	294	290
B_2O_3	0.0133	298	295
Al_2O_3	0.015	314	313
SiO_2	0.030	307	303
PbO	0.030	273	276
Fe_2O_3	0.015	314	311
CaO	0.030	314	313
NiO	0.030	313	311
Mn_2O_3	0.030	312	310
Mn_2O_3	0.041	320	319
TiO_2	0.030	301	300
V_2O_5	0.015	235	236
ZrO_2	0.030	318	315
CeO_2	0.030	318	315
CaF_2	0.030	308	304

TABLE VII. 6—Surface Tension and Composition of Some Analyzed Commercial Glasses

After Badger, Parmelee and Williams

	A	B	D	E	F	G
		Surface tension (dynes/cm.)				
At 1200°	303	247	302	304	313	318
At 1350°	302	245	299	300	314	315
		Batch Composition				
SiO_2	74.1	65.35	72.56	74.52	70.74	72.50
B_2O_3			1.00			
Na_2O	16.65	5.70			13.11	13.59
K_2O	0.04	8.40				
CaO	4.65	0.21	4.02	4.35	13.72	9.24
MgO	3.23	0.03	2.54	3.18	0.12	3.00
BaO		1.40		0.99		
PbO		17.50				
Al_2O_3	0.33	0.18				1.06
Fe_2O_3	0.065	0.049				0.09

A. National Bureau Standards Glass No. 80. Also contains: SO_3, 0.41; As_2O_3, 0.03; As_2O_5, 0.07; Cl, 0.047; TiO_2, 0.02; ZrO_2, 0.003; MnO, 0.003. Ignition loss, 0.30.

B. National Bureau Standards Glass No. 89. Also contains: P_2O_5, 0.23; SO_3, 0.03; As_2O_3, 0.03; As_2O_5, 0.36; Cl, 0.05; TiO_2, 0.01; ZrO_2, 0.005; MnO, 0.088. Ignition loss, 0.32.

D. Alkalies, 16.30; R_2O_3, 3.58.

E. Alkalies, 16.51; R_2O_3, 0.33.

F. R_2O_3, 0.33; Na_2SO_4, 0.58; As_2O_3, 0.25; NaCl, 0.86.

G. Na_2SO_4, 0.41; NaCl, 0.11.

no explanation could be given for the difference between them. A similar difference was observed with B_2O_3; the bubble method gave 87.7 at 830°, 87.2 at 900°, and the fiber method gave 32.7.

TABLE VII. 7—Surface Tensions Measured by the Fiber and Bubble Methods, and Batch Composition of the Glasses Used by Keppeler

	Surface tension (dynes/cm.)					
Fiber method	163.7	152.5	147.1	141.9	135.4	129.2
Bubble method	321.3	310.9	301.8	301.1	288.5	277.8
	Batch Composition					
SiO_2	75.98	74.38	72.88	70.88	68.38	65.88
B_2O_3		1.50	3.00	5.00	7.50	10.00
Na_2O	13.84	13.84	13.84	13.84	13.84	13.84
CaO	8.93	8.93	8.93	8.93	8.93	8.93
R_2O_3	1.35	1.35	1.35	1.35	1.35	1.35

Pietenpol[25] used a "bulb" method, in which the excess of pressure inside a bulb, supported inside a furnace, is measured with a manometer. The "approximate" compositions of the glasses used are given in Table VII. 8, and the experimental results in Figs. VII. 3 and VII. 4. Glass No. 10 was an alkali-free borosilicate, of undetermined composition, density 2.82. The curves that represent the change of surface tension with temperature show a rapidly "descending branch corresponding to the range of temperature where softening of the glass takes place, and a more nearly horizontal portion extending over the higher range of temperature. * * * It is, however, quite obvious that the high values shown in the curves at low temperatures cannot be interpreted as indicating the true values of surface tension. Here the rigidity or high viscosity of the glass may be such as to mask very largely the effect of the force of surface tension."

TABLE VII. 8—Approximate Composition of Glasses Measured by Pietenpol

No.	3	4	6	7	8
SiO_2	62.5	57.5	63.0	81.0	67.0
B_2O_3				12.5	2.0
Na_2O	9.0	4.2	8.0	4.25	14.0
K_2O	6.0	8.0	6.0		
CaO	0.5	0.4			7.0
MgO	0.5	0.4			
ZnO					7.0
PbO	21.0	28.6	22.0		
Al_2O_3	0.8	1.4	1.0	2.0	2.5
Fe_2O_3	0.2	0.2			
Density	3.34	3.50	3.21	2.28	2.66

The most comprehensive study of the surface tension of glass is that

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[25] Pietenpol, W. B., *Physics*, 7, 26 (1936).

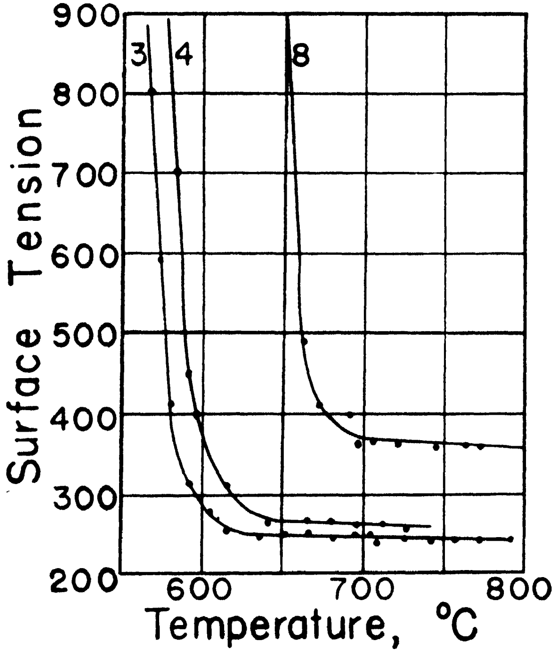

FIGURE VII. 3.—Change of Surface Tension in Dynes per Cm. with Temperature of Melts of Compositions given in the Text. After Pietenpol.

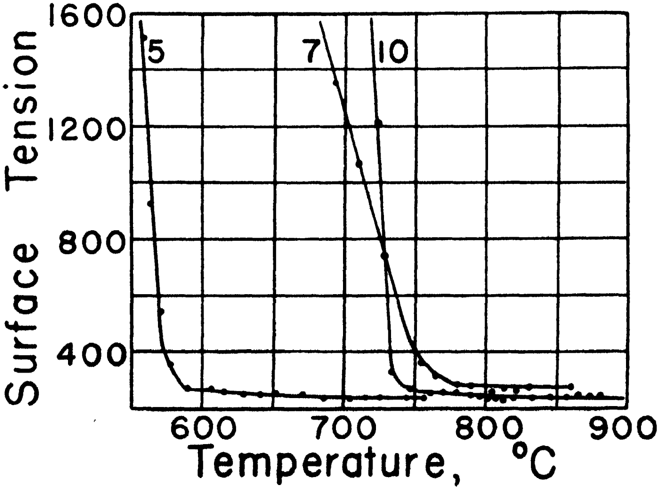

FIGURE VII. 4.—Change of Surface Tension in Dynes per Cm. of Melts of Compositions given in the Text. After Pietenpol.

TABLE VII. 9—The Surface Tension of Some Glasses in the System Na_2O-CaO-SiO_2

After Washburn, Shelton, and Libman

Glass No.	SiO_2	Na_2O	CaO	Surface Tension (dynes per cm.) 1206° C.	1454° C.	$\frac{\Delta\gamma}{\Delta t}$
2	82.6	17.4			153.7	
3	70.0	30.0		164.0	148.8	0.061
4	60.0	40.0		156.1	153.6	0.010
5	63.0	13.6	23.4	164.1	158.7	0.022
6	60.5	20.0	19.5	159.6	128.0	0.013
7	68.1	21.9	10.0	150.0	145.9	0.0165
8	70.0	20.0	10.0	153.6	140.4	0.054
9	54.25	38.0	7.75	165.4	153.7	0.047
10	70.0	10.0	20.0	164.0	156.4	0.031
12	72.25	15.1	12.1		151.6	0.030
13	73.5	16.5	10.0	166.9	159.4	0.030
15	67.5	15.5	17.0	158.7	145.4	0.0546
16	64.95	19.3	15.75	150.1	138.6	0.0465

of Washburn, Shelton, and Libman[26] on the system Na_2O-CaO-SiO_2. The method used was a modification of Wilhcmg's dipping plate method, in which a platinum cylinder, suspended from a Joly balance, is first

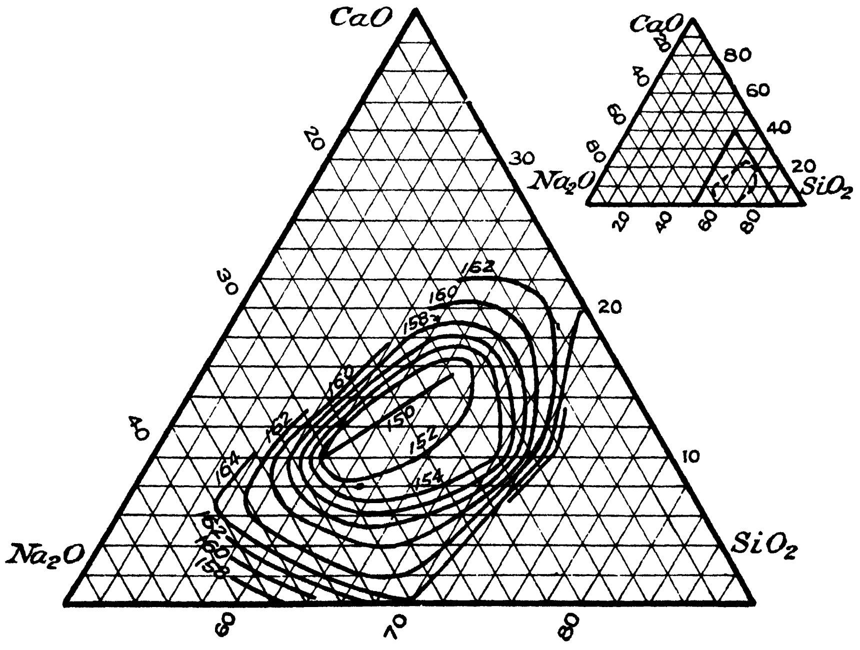

FIGURE VII. 5.—Surface Tension in Dynes per Cm. of Melts in the System Na_2O-CaO-SiO_2 at 1206° C. After Washburn, Shelton and Libman, with Sequence of Components altered.

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[26] Washburn, E. W., Shelton, G. R., and Libman, E. E., *Univ. Ill. Eng. Expt. Sta. Bull.*, **140**, 71 pp. (1924).

weighed in air, after which the molten glass is raised until its surface just touches the lower end of the cylinder, which immediately sinks into the liquid. The surface tension can be calculated from the readings of the Joly balance, the dimensions of the cylinder, the density of the liquid glass, and a calibration constant for the apparatus. By a slight modification of the method the density can be eliminated from the equations.

Measurements were made at 1206° C. and at 1454° C on the series of glasses of compositions given in Table VII. 9; results are given in Table VII. 9, and in Fig. VII. 5. The change in surface tension with temperature was determined from 1200° to 1454° C. for glass 16, and is represented in Fig. VII. 6. The surface tension increased very slightly with decreasing temperature, the temperature coefficient ranging from −0.01 per cent to −0.04 per cent per degree.

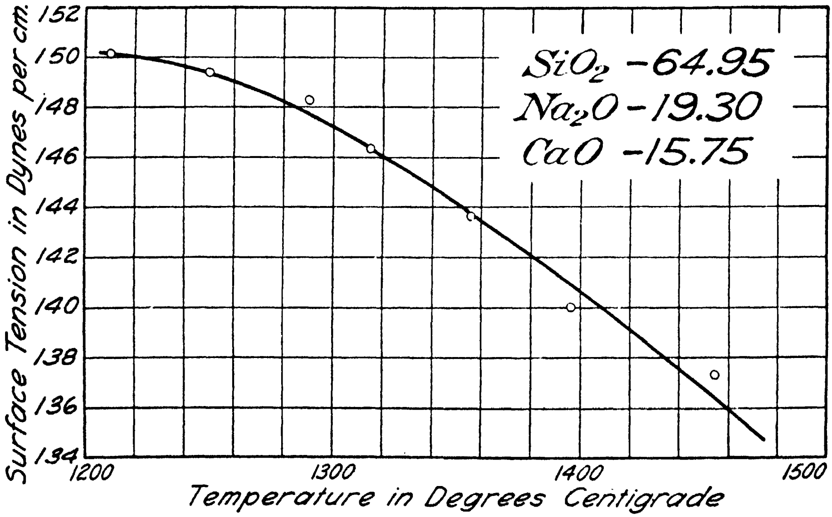

FIGURE VII. 6.—Change of Surface Tension in Dynes per Cm. with Temperature. After Washburn, Shelton and Libman.

There is a discrepancy among the various observers far greater than can be explained by differences in composition or in temperature. The values obtained for silicate glasses range from about 128 to 167 dynes per cm., obtained by Washburn, Shelton, and Williams, to about 400 to 500 dynes per cm., obtained by Lecrenier. Keppeler obtained values of surface tension by the fiber elongation method about one-half of those obtained by the bubble pressure method, a difference probably caused by failure of the theory on which the fiber elongation is based. At present the best values of surface tension of ordinary silicate glasses are near

300 dynes per cm. All observers agree on the low temperature coefficient of surface tension, from −0.01 per cent to −0.04 per cent per degree C.

The results of Washburn, Shelton, and Libman probably are consistent among themselves, and since they found a minimum of surface tension within the component triangle, it follows that addition of any one of the components to this minimum composition raises the surface tension; conversely, by appropriate choice of the original glass, addition of any one of the components will lower the surface tension. In multicomponent systems great care must be taken in generalizing from insufficient evidence; nevertheless, it may be said that borates and lead glasses have a lower surface tension than alkali or alkaline earth silicates. More systematic work is needed, and in such work it should be remembered that a single linear variation in composition in a system of several components does not permit generalizations as to the system as a whole.

Chapter VIII

The Heat Capacity of Glass

The true heat capacity of a substance is the slope of the curve giving the heat content per unit of mass as a function of temperature, at the temperature in question; the quantity of heat per unit of mass required to produce a small rise in temperature; $c = dQ/dt$. The quantity usually measured is the mean heat capacity, the ratio between a large increment in temperature of unit mass and the quantity of heat required to produce that increment. It is equivalent to the slope of a straight line joining the two temperatures on the curve of heat content versus temperature. The measurement may be made at constant pressure or constant volume, and the resulting heat capacity is that at constant pressure, c_p, or at constant volume, c_v.

The heat capacity is usually stated in joules, the absolute energy unit; when expressed in calories per gram, heat capacity becomes specific heat, the ratio of the heat capacity of the substance to that of water under specified conditions. One gram-calorie (mean) = 4.186 absolute joules; one gram-calorie (20°) = 4.181 joules; one gram-calorie (15°) = 4.185 joules.

TABLE VIII. 1—Factors for Calculation of the Specific Heat of Glass

After Winkelmann

SiO_2	0.1913	Na_2O	0.2684	CaO	0.1903	PbO	0.0512
B_2O_3	0.2272	K_2O	0.1860	BaO	0.0673	MgO	0.2439
P_2O_5	0.1902	Li_2O	0.5497	ZnO	0.1248	Al_2O_3	0.2074

Specific heat is sometimes expressed in British units; one British Thermal Unit (B. T. U.) is the heat required to raise one pound of water one degree F. One B. T. U. (mean) = 1054.8 joules = 251.98 cal. (mean); one B. T. U. (60° F.) = 1054.6 joules; one B. T. U. (39° F.) = 1060.4 joules.

Heat capacity is generally assumed to be approximately additive, both for crystals and for liquid mixtures, although it is well known that precise measurements show departures from the additive relationship, the cause of which is considered to be well understood. The specific heat of glasses is more nearly additive than any other quantity. This was shown by Winkelmann,[1] who measured the specific heat, in

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[1] Winkelmann, A., *Ann. Physik Chem.*, **49**, 401 (1893).

the temperature range of approximately 0° to 100°, of a number of glasses whose compositions were not accurately known, and obtained results which agreed to within one to two per cent of those calculated from the composition, using the factors for the several oxides given in Table VIII. 1. Most of these are factors previously published by Regnault,[2] which were deduced from measurements on crystalline compounds. A real study of the specific heat of glass is greatly to be desired, not only for its practical importance, but also for its application to the problem of the constitution of glass.

Thuret[3] discussed the representation of specific heat data as a function of temperature, and gave formulas for alumina, calcium oxide and vitreous silica, from −200° to +2600°. The mean specific heat is given by a formula of the type

$$c_m = \frac{at - c_o}{bt - 1},$$

and the true specific heat by

$$c = \frac{abt - 2at - c_o}{(bt - 1)^2}$$

Values adopted for a, b, and c_0, respectively, were: Al_2O_3, 0.5946×10^{-3}, 1.964×10^{-3}, 0.1801; CaO, 0.4792×10^{-3}, 1.84×10^{-3}, 0.1736; SiO_2 (vitreous), 0.4579×10^{-3}, 1.4747×10^{-3}, 0.1683.

One-Component Glasses

Boric Oxide, B_2O_3. Thomas and Parks[4] used a "radiation" calorimeter, which gave true heat capacity at constant pressure. The 18-gram sample was prepared by heating it in a platinum crucible for eight hours at about 900° C., and pouring it into the silver calorimeter, maintained at about 500°, then cooling to 50° C. in about half an hour. The heat capacity of this quickly cooled glass was then measured in a continuous series of observations, from 33° to 345°, in about 14 hours. The sample was then cooled, the process requiring 18 hours, and a second series of heat capacity measurements was made during cooling from 332° to 112°. The heat capacity of this slowly cooled glass was then determined "by heating it up gradually from 35° to 325° C." The results of the three series of determinations are assembled in Fig. VIII. 1. There was a rapid increase in heat capacity in the softening region of the glass. The two curves obtained on heating show a hump just before flattening out, but the curve obtained on cooling shows a smooth transition from the higher to the lower heat capacity.

The heat capacity values are represented by the equation: $c_p = 0.00046t + 0.199$ to within one unit in the last decimal place up to

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[2] Regnault, H. V., *Ann. Chem. Phys.*, **1**, 129 (1841).

[3] Thuret, A., *J. Soc. Glass Tech.*, **20**, 680 (1936).

[4] Thomas, S. B., and Parks, G. S., *J. Phys. Chem.*, **35**, 2091 (1931).

130° for the curve obtained by heating the sample obtained by slow cooling, and up to 100° with the sample obtained by rapid cooling; and the same equation represents the results obtained during cooling up to 161°. They were usually reproducible to 0.5 per cent or better, and the estimate of absolute accuracy of two per cent at 100° and four per cent at 350° was considered conservative.

The measurements were made with continuously changing temperatures, and if glasses in the highly viscous condition below the softening point require periods of time which increase with decreasing temperature to reach the equilibrium condition characteristic of the temperature of the measurement, then it is probable that the glasses measured were not in equilibrium at temperatures below that of the "hump." The measurements are a quantitative corroboration of the earlier observations by Tool and his co-workers,[5] and likewise show that, when a glass is heated below the upper part of the annealing region at a rate too rapid for equilibrium to be attained, the stored-up lag is suddenly released when the viscosity becomes small enough, producing a discontinuity. It would be useful to have heat capacity measurements made below the softening point, with heat treatment prolonged at each temperature until a demonstrated constant condition was reached, before the measurement was made. It is probable that there would not be a hump on the heat capacity curve so obtained.

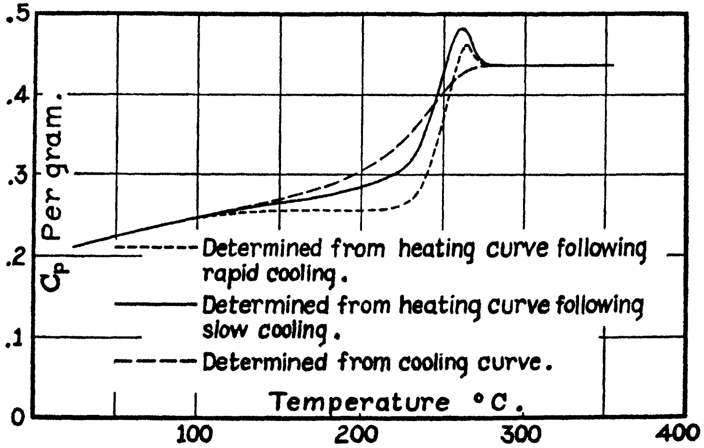

FIGURE VIII. 1.—Curves of Heat Capacity for Boric Oxide Glass. After Thomas and Parks.

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[5] Tool, A. Q., and Valasek, J., *Sci. Papers Bur. Standards*, **358**, 537 (1920). Tool, A. Q., and Eichlin, C. G., *J. Optical Soc. Am.*, **4**, 340 (1920). Tool, A. Q., and Eichlin, C. G., *J. Am. Ceram. Soc.*, **8**, 1 (1925). Tool, A. Q., and Eichlin, C. G., *J. Research Natl. Bur. Standards*, **6**, 523 (1931); *J. Am. Ceram. Soc.*, **14**, 276 (1931).

Silica, SiO$_2$. Sosman[6] discussed the experimental data on the heat capacity of vitreous silica, and gave the most probable values in a table, reproduced as Table VIII. 2. Both the true heat capacity, c_p, and the mean heat capacity, c_m, are given. Sosman remarked (p. 314): "The slight irregularity in the curve for vitreous silica at about 500 to 700° C. may not be real, but due to the form of curve resulting from the averaging of several curves of mean heat which do not agree particularly well. Furthermore, it is entirely possible, and even probable, that the true heat capacity of vitreous silica varies with its previous history, just as do its elastic properties, but there have been no experiments to test this question. On the other hand, there are suggestions here and there of a genuine irregularity in vitreous silica near 600°."

TABLE VIII. 2—True Heat Capacity and Mean Heat Capacity from 0° C. of Vitreous Silica*

After Sosman

t, ° C.	c_p	c_m	t, ° C.	c_p	c_m
−255	4.8		400	260	222
−250	7.7	93.6	450	266	227
−243	12.7		500	270	231
−233	19.8		550	273	235
−223	26.7		600	275	238
−200	43.4	110.1	700	281	244
−150	79.5	126	800	286	249
−100	112.8	141	900	289	253
− 50	142.2	154.5	1000	292	257
0	165.7	165.7	1100	294	260
50	185	176	1200	303	263
100	201	185	1300	316	267
150	215	193	1400	328	270
200	227	200	1500	339	275
250	236	206	1600	346	279
300	245	212	1700	352	283
350	254	212			

* Values are 10^3 c_p or c_m in 20° calories per gram.

Multi-Component Glasses

There has been no systematic study of the dependence of the heat capacity of glass upon composition. The results of Winkelmann,[1] obtained in his classic study of the heat capacity of a series of experimental and commercial glasses, are included in Table I. 2. Measurements on glasses of unknown composition have been made by Magnus,[7] Nernst,[8] Koref,[9] Borisfield,[10] and Schultz.[11]

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[6] Sosman, R. B., "The Properties of Silica," Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

[7] Magnus, A., *Ann. Physik*, **31**, 597, 606 (1910).

[8] Nernst, W., *Sitzber. kgl. preuss. Akad. Wiss.*, **12**, **13**, 261 (1910); *Ann. Physik*, **36**, 395 (1911).

[9] Koref, F., *Ann. Physik*, **36**, 49, 64 (1911).

[10] Borisfield, *Trans. Roy. Soc. (London), A*, **211**, 199 (1911).

[11] Schultz, K., *Zentr. Mineral., Geol.*, **1911**, 632.

Parmelee and Badger[12] made measurements by the dropping method, using silica glass to standardize their apparatus. The absolute accuracy was judged to be plus or minus one per cent. The results are summarized in Table VIII. 3. Glasses 1 and 8 were standard samples from the Bureau of Standards, and 9 was an opal glass from the same source.

TABLE VIII. 3—Heat Capacity of Some Commercial Glasses *

After Parmelee and Badger

	Composition									Heat Capacity	
No.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	MgO	PbO	Al_2O_3	Fe_2O_3	40–800°	40–1000°
1[a]	74.1		16.65	0.04	4.65	3.23		0.33	0.065	0.280	0.292
2[b]	71.88		17.59		5.01	3.64		1.21	0.07	0.268	0.290
3[c]	73.28		16.31		5.31	3.88		0.48		0.280	0.285
4	74.95		15.82		4.79	3.30		1.13		0.265	0.293
5[d]	71.58		14.00		12.94	0.10		0.54	0.12	0.274	0.289
6[e]	74.84		16.48		2.55	1.77		4.36		0.279	0.281
7[f]	61.91		8.32	6.19	tr.	tr.	22.23	1.00	0.15	0.211	0.224
8[g]	80.1	12.6	4.17	0.15		0.02		1.92	0.077	0.271	0.287
9[h]	67.53		8.48	3.25	10.48		0.097	6.01	0.081		0.269

* Values are in 20° calories per gram per ° C.

[a] TiO_2, 0.02; ZrO_2, 0.003; MnO, 0.003; SO_3, 0.41; As_2O_5, 0.07; As_2O_3, 0.03; Cl, 0.047; loss on ignition, 0.30. Additional heat capacity values; from 40°; 850°, 0.285; 900°, 0.287; 950°, 0.288; 1050°, 0.298.

[b] SO_3, 0.41; As_2O_3, 0.20.

[c] BaO, 0.24.

[d] Na_2SO_4, 0.66; NaCl, 0.06.

[e] Fe_2O_3 is probably less than 0.1%.

[f] As_2O_3, 0.20.

[g] TiO_2, 0.026; ZrO_2, 0.014; As_2O_3, 0.09; As_2O_5, 0.14; SO_3, 0.01; Cl, 0.03; loss on ignition, 0.67.

[h] ZnO, 0.08; TiO_2, 0.019; ZrO_2, 0.0095; As_2O_5, 0.102; As_2O_3, 0.091; P_2O_5, 0.22; Cl, 0.014; F, 5.72.

2 was a glass used for electric light bulbs, 3, a bottle glass, 4, a milk bottle glass, 5, a plate glass, and 6 was a lead glass of the type sometimes used for electric light bulbs. 5 and 8 showed some devitrification, and 9 was greatly altered in appearance by quenching.

Schwiete and Wagner[13] measured the mean specific heats of three glasses having the following compositions:

	SiO_2	Alkalies	CaO	Al_2O_3	Fe_2O_3	Mn_3O_4
a	64.32	12.44	12.85	7.52	1.90	0.44
b	66.1	12.59	12.2	6.03	1.27	1.40
c	62.8	8.64	12.7	7.1	1.22	7.06

The method of mixtures was used, and the results are given in Table VIII. 4 both from 0° and from 18° to an upper temperature.

Hildebrand, Duschak, Foster, and Beebe[14] measured the interval specific heat of "Pyrex" laboratory glass. Measurements were made in

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[12] Parmelee, C. W., and Badger, A. E., *Univ. Ill. Eng. Expt. Sta. Bull.*, No. 271, (1934).

[13] Schwiete, H. E., and Wagner, H., *Glastech. Ber.*, 10, 26 (1932).

[14] Hildebrand, J. H., Duschak, A. D., Foster, A. H., and Beebe, C. W., *J. Am. Chem. Soc.*, 39, 2293 (1917).

TABLE VIII. 4—Mean Specific Heats of Three Glasses from 0°, and from 18°, to the Indicated Upper Temperatures

After Schwiete and Wagner

Upper Temperature (° C.)	Glass *a*		Glass *b*		Glass *c*	
	18°	0°	18°	0°	18°	0°
300	0.2238	0.2216	0.2284	0.2258	0.2169	0.2147
500	0.2399	0.2379	0.2400	0.2380	0.2326	0.2307
700	0.2562	0.2544	0.2602	0.2583	0.2520	0.2501
900	0.2707	0.2691	0.2779	0.2760	0.2675	0.2657
1100	0.2751	0.2737	0.2798	0.2782	0.2699	0.2684
1300	0.2880	0.2866	0.2912	0.2897	0.2838	0.2823

the intervals 20° to 100°, 20° to 135°, 20° to 200°, and 20° to 265° C., with the results represented by the formula

$$c_t = 0.174 + 0.00036t$$

where c_t denotes specific heat at t °C.

TABLE VIII. 5—True Specific Heat of Lindemann Glass

After Simon

t (abs)	24.3	31.0	36.0	45.2	48.3	25.3
c_p	0.0084	0.0123	0.0154	0.0239	0.0257	0.0290
t (abs)	85.6	88.3	97.6	99.5	112.3	114.8
c_p	0.0634	0.0653	0.0737	0.0771	0.0884	0.0911

De Vries,[15] using an electrical method, determined the heat capacity of "Pyrex" glass from 26° to 173° C. His results are represented by the formula

$$\text{Heat capacity} = 0.1839 + 0.0003134\ (t - 20).$$

TABLE VIII. 6—Mean Specific Heats of Silicate Glasses

After White

Glass	G. cal.$_{15°}$ per ° C.					
	0–100°	0–300°	0–500°	0–700°	0–900°	0–1100°
Anorthite, An $CaO\cdot Al_2O_3\cdot 2SiO_2$	0.1881	0.2152	0.2306	0.2406		
Andesine, $Ab_1\ An_1$	0.1932	0.2211		0.2484	0.2615	
Albite, Ab $Na_2O\cdot Al_2O_3\cdot 6SiO_2$	0.1977	0.2238	0.2410		0.2640	
Microcline $K_2O\cdot Al_2O_3\cdot 6SiO_2$	0.1919	0.2163	0.2321	0.2431	0.2515	0.2598
Wollastonite $CaO\cdot SiO_2$	0.1852	0.2078	0.2208	0.2355		
Diopside $CaO\cdot MgO\cdot 2SiO_2$	0.1938	0.2189	0.2333	0.2439		
Magnesium metasilicate $MgO\cdot SiO_2$	0.2040	0.2302	0.2474	0.2598		

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[15] De Vries, T., *Ind. Eng. Chem.*, **22**, 617 (1930).

Simon[16] measured the true heat capacity of "Lindemann glass,"[17] $10\,Li_2B_2O_7 + 2\,BeO + 3\,B_2O_3$, by the Nernst method from 24° to 115° A., with the results given in Table VIII. 5.

White[18] measured the specific heat of "soft glass" and of several mineral glasses by the method of mixtures. His results, probably the most accurate in the literature, are given in Table VIII. 6.

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[16] Simon, F., *Ann. Physik*, **68**, 241 (1922).

[17] Lindemann, Ch. L., and F. A., *Z. Roentgenkunde*, **13**, 141 (1911).

[18] White, W. P., *Am. J. Sci.*, **2**, 334 (1909); *Am. J. Sci.*, **47**, 1 (1919).

Chapter IX

The Thermal Conductivity of Glass

The rate at which heat energy is transmitted through glass by conduction depends on the size and shape of the conducting path, on the difference in temperature between the two faces, and on the composition of the glass. The thermal conductivity usually is measured by the plate method, in which the sample is placed between the two plates of good thermal conductivity, to one of which heat is supplied at a known constant rate, while from the other heat is removed. Edge effects are eliminated by a guard ring. When a steady state is reached, the temperature gradient is measured. Thermal conductivity commonly is expressed in calories per square centimeter per second per degree Centigrade per centimeter. In some engineering calculations English units are used, and thermal conductivity is expressed in B. T. U. per square foot per hour per degree Fahrenheit per inch. The factors for changing thermal conductivity, using calories as heat units, to joules are the same as for changing specific heat, namely, 1 calorie (15° C.) cm.^{-2} sec.^{-1} (deg. C., $\text{cm.}^{-1})^{-1}$ = 4.185 joules (abs.) cm.^{-1} sec.^{-1} (deg. C., $\text{cm.}^{-1})^{-1}$. One calorie (15° C.) cm.^{-2} sec.^{-1} (deg. C., cm.^{-1}) = 1.225 B. T. U. (39°) ft.^{-2} sec.^{-1} (deg. F., in.^{-1}). One B. T. U. (39°) ft.^{-2} sec.^{-1} (deg. F., in.^{-1}) = 5.218 joules (abs.) cm.^{-1} sec.^{-1} (deg. C., $\text{cm.}^{-1})^{-1}$. Thermal diffusivity is the thermal conductivity divided by the product of density and specific heat.

In many problems concerning the transfer of heat, the thermal conductivity of the materials is a less important factor than the "skin effect" of thin films. Littleton and Bates[1] found that, although copper has a thermal conductivity coefficient 300 times that of glass, new copper condenser tubes condense only 2.5 times as much steam as glass tubes, and the difference is smaller when the copper tubes become slightly corroded. Radiation is another factor in heat transfer problems which is frequently overlooked, and may be of greater importance than thermal conduction. This factor becomes of increasing importance as temperature is increased; and at higher temperatures we have no knowledge of the thermal conductivity of glass.

Thermal conductivity is usually considered to be additive, but the experimental data are not sufficient to confirm the assumption. There has been little systematic study of thermal conductivity of glass in its

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[1] Littleton, J. T., and Bates, H. C., *Chem. Met.*, 39, 315 (1932).

dependence on composition, and much of the experimental work has been on multicomponent glasses. Paalhorn[2] measured the thermal conductivity of the glasses studied by Winkelmann and proposed factors for the calculation of conductivity from composition, which agreed fairly well with his observed values. Later, Focke,[3] working with similar glasses, obtained results differing by as much as 40 per cent from those of Paalhorn, and proposed new factors. Probably the best work is that of Eucken,[4] who determined the thermal conductivity of silica glass and of a number of optical glasses, summarized in Table IX. 1. The glasses were not analyzed, so that compositions must be inferred from the optical properties of the type glass. Eucken emphasized the difference between the thermal conductivity of a crystalline substance, such as quartz, which increases with decreasing temperature and reaches a high value below the temperature of liquid air, and that of a glass, which decreases with falling temperature.

TABLE IX. 1—Thermal Conductivity * of Silica Glass and of Some Optical Glasses

After Euchen

Glass No., Table III. 4	Glass Type	−190°	−78°	0°	100°
—	Silica	1.58	2.77	3.32	4.57
1	469/649	1.181	2.532	2.796	3.243
8	516/640	1.195		2.825	
a	519/604	1.182		2.675	
36	613/369	0.865		1.900	
40	649/338	0.851		1.867	
43	754/275	0.807		1.698	1.812
70	516/692	0.877		1.769	2.007

* Values are in 10^{-3} cal. cm^{-2} sec^{-1} (° C., $cm^{-1})^{-1}$.

a Borosilicate Crown O 3453; SiO_2, 68.5; B_2O_3, 3.5; Na_2O, 12; K_2O, 5; ZnO, 1.0; BaO, 9.7; As_2O_3, 0.3.

Russ,[5] a pupil of Eucken, measured the thermal conductivity of glasses prepared by Gehlhoff and Thomas (cf. p. 160). The glasses were not analyzed. His results are assembled in Table IX. 2. He discussed the calculation of thermal conductivity from composition, and adopted Winkelmann's formula

$$\frac{100}{\lambda} = \frac{b_1}{\lambda_1} + \frac{b_2}{\lambda_2} + \cdots\cdots + \frac{b_n}{\lambda_n}$$

in which λ is the reciprocal of the thermal conductivity; and λ_1, λ_2, . . . λ_n, constants for the various components whose percentages by volume are given by b_1, b_2, . . . b_n. Values of constants for the various

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[2] Paalhorn, O., Diss., Jena, 1894. Quoted in Hovestadt, H., "Jena Glass," translated by Everett, J. D. and A., Macmillan, New York, 1902.

[3] Focke, T. M., *Ann. Physik*, **67**, 132 (1899).

[4] Eucken, A., *Ann. Physik*, **34**, 185 (1911).

[5] Russ, A., *Sprechsaal*, **61**, 887 (1928).

TABLE IX. 2—Thermal Conductivity * of Some Experimental Glasses

After Russ

1. *Series 18% Na_2O, 82% ($SiO_2+B_2O_3$)*

Weight % B_2O_3	0°	100°
5	2.428	2.670
10	2.411	2.568
15	2.352	2.568
20	2.327	2.528
30	2.248	2.478

2. *Series 20% PbO, 80% (SiO_2+Na_2O)*

% Na_2O		
10	2.264	2.455
15	2.119	2.353
20	2.021	2.279
25	1.980	2.063

3. *Series 20% PbO, 80% (SiO_2+K_2O)*

% K_2O		
15	1.940	2.146
20	1.813	2.035

4. Series *18% Na_2O, 82% (SiO_2+MgO)*

% MgO		
5	2.368	2.612
8	2.419	2.644
10	2.327	2.553
12	2.282	2.460
15	2.270	2.453
18	2.271	2.447

5. *Series 18% Na_2O, 82% (SiO_2+CaO)*

% CaO		
5	2.228	2.491
10	2.172	2.426
15	2.162	2.320

6. *Series 18% Na_2O, 82% (SiO_2+ZnO)*

Weight % ZnO	0°	100°
5	2.386	2.606
10	2.213	2.326
15	2.150	2.321
20	2.024	2.210
30	1.928	2.094

7. *Series 18% Na_2O, 82% (SiO_2+BaO)*

% BaO		
5	2.258	2.457
10	2.201	2.398
15	1.967	2.194
25	1.908	2.110

8. *Series 18% Na_2O, 82% (SiO_2+PbO)*

% PbO		
5	2.153	2.355
10	2.151	2.356
20	2.090	2.297
25	2.018	2.221

9. *Series 18% Na_2O, 82% ($SiO_2+Al_2O_3$)*

% Al_2O_3		
3	2.322	2.582
6	2.301	2.559
9	2.293	2.461
12	2.261	2.450

10. *Series 18% Na_2O, 82% ($SiO_2+Fe_2O_3$)*

% Fe_2O_3		
5	2.208	2.530
10	2.250	2.474
15	2.191	2.504
20	2.133	2.345

* Values are 10^{-3} g-cal cm^{-2} sec^{-1} (° C., cm^{-1})$^{-1}$.

oxides are given in Table IX. 3, together with factors for the calculation of density used by Russ. These density factors do not represent new determinations.

Bridgman[6] measured the thermal conductivity of Pyrex chemical resistant glass as a function of pressure, and found it to be represented, at both 30° and 75° C., by the expression:

$$\text{Thermal conductivity} = 0.00261 + 0.00001\ (p/1000).$$

The experiments extended up to pressures of 12,000 kg./cm.^{2}

Stephens[7] measured the change in thermal conductivity with tem-

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[6] Bridgman, P. W., *Am. J. Sci.*, (5) **7**, 81 (1924).

[7] Stephens, R. W. B., *Phil. Mag.*, (7) **14**, 897 (1932).

TABLE IX. 3—Factors for the Calculation of Thermal Conductivity and Density

After Russ

Oxide	Density Factor	Thermal Conductivity Factor
SiO_2	2.30	3.00
B_2O_3	2.35	3.70
Na_2O	3.20	10.70
K_2O	2.90	13.40
CaO	3.90	8.80
BaO	7.10	11.85
ZnO	5.90	8.65
PbO	10.00	11.70
MgO	3.90	4.55
Al_2O_3	3.20	6.25
Fe_2O_3	3.87	

perature of Pyrex chemical resistant glass from −181° to +250° C. His results are represented by the equation:

$$K = A + b \log_{10} T,$$

in which K is the thermal conductivity, T is the absolute temperature, and A and b are empirical constants, which have the values −0.003523 and +0.002454, respectively. At 20° the experimental value of thermal conductivity was 0.00245; at 90°, 0.00277.

Chapter X

The Density of Glass

Density is the property of glass most frequently measured, and determinations too numerous to mention have been recorded of individual glass densities incidental to another research. The composition of the glass was usually unknown and not pertinent, and the densities so recorded are devoid of general interest. Many standard types of glass, such as Jena 59^{III} or Pyrex resistant laboratory ware, are of such widespread use that knowledge of their density is frequently needed. Fortunately, such glasses ordinarily are constant enough in composition for the density commonly given to be used for all but the most exacting work. Densities of many commercial glasses are given in Tables I. 2, XVI. 22, and XVI. 23.

There is also a great mass of measurements obtained on simpler glasses, usually in systematic studies of the variation of property with composition, made in the hope that information would be obtained pertinent to the problem of the constitution of glass. This hope has not been justified, but there has resulted a large body of more or less systematic data. The composition sometimes is known only approximately from the batch composition; sometimes it is known precisely. Such studies have been included whenever possible.

Additive Relationship

The specific volume of glass approximates to an additive property of its constituent oxides, a fact which has long been recognized and which frequently has been expressed by assigning to each oxide a factor, by the use of which the specific volume may be calculated roughly by means of a formula of the type:

$$\frac{100}{D}=\frac{x'}{d'}+\frac{x''}{d''}+\ \cdot\ \cdot\ \cdot\ +\frac{x^n}{d^n}$$

in which $x', x'', \ldots x^n$ are the percentages by weight of the components, and $d', d'', \ldots d^n$ are the corresponding factors. The factors given by several authors are assembled in Table X. 1. Another set of factors is in Table IX. 3.

This additive relationship, which is true in general of all liquids, has long been known. Within the narrow composition range of most soda-lime-silica glasses, calculation of density by means of additive factors should give a fair approximation to the correct values. The reason is evident from inspection of Fig. X. 5. The lines of constant density are not straight; but within the range of composition from 70 to 80 per cent SiO_2, from 0 to 15 per cent CaO, the departures from straight lines are not as great as the differences which may be caused by differences in annealing. The low density of silica is the dominant factor. Additions of small amounts of most of the other common ingredients cause changes in density which are small, because the other common oxides are not greatly different in density. When the amounts of the added oxides are large, or when they are of greatly differing density, the effect on the curvature becomes apparent. The differences, however, rarely extend to the first decimal place.

TABLE X. 1—Factors for Calculating Density from Composition *

Oxide	Winkelmann and Schott [1]	Baillie [2]	English and Turner [3]	Tillotson [4]
SiO_2	2.3	2.24	2.20	2.3
B_2O_3	1.9			
Na_2O	2.6	3.20	3.47	
K_2O	2.8			
MgO	3.8	3.25	3.38	4.0
CaO	3.3	4.30	5.00	4.1
ZnO	5.9			
BaO	7.0			
PbO	9.6			
Al_2O_3	4.1	2.75	2.75	2.75
P_2O_5	2.55			
Li_2O				3.7

* Values given are of d', etc., in $\frac{100}{D} = \frac{x'}{d'} + \frac{x''}{d''} + \ldots + \frac{x^n}{d^n}$.

[1] Winkelmann, A., and Schott, O., *Ann. Physik Chem.*, **51**, 730 (1894); Hovestadt, H., and Everett, J. D. and A., "Jena Glass," Macmillan and Co., London, 1902.

[2] Baillie, W. L., *J. Soc. Chem. Ind.*, **40**, 141 (1921).

[3] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **6**, 228 (1922).

[4] Tillotson, E. W., Jr., *J. Ind. Eng. Chem.*, **3**, 897 (1911).

In speculation as to the reasons for this additive feature, and for the departures from the additive relationship, the assumption frequently is made that definite compounds exist in the glass, and that when the composition is expressed in terms of these compounds, the relationship between density and composition will be truly linear. As long as only a single binary compound of each oxide is assumed to combine with silica, the assumption of such compound formation is equivalent to assuming a density for the combining oxide. This was pointed out by Morey and Merwin [1] for binary glasses, and the argument is easily extended to other cases. For example, assumption of the compounds $Na_2O \cdot 2SiO_2$ and $CaO \cdot SiO_2$ in the ternary system Na_2O-CaO-SiO_2 is equivalent to passing a plane through the three points corresponding to the densities of

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[1] Morey, G. W., and Merwin, H. E., *J. Optical Soc. Am.*, **22**, 632 (1932).

these two compounds and of silica glass in the model representing density. Extension of this plane to its intersections with the edges Na_2O and CaO gives the values assumed for these oxides in the calculation. Proof of the extension of this self-evident proposition to systems of more components should not be necessary. Several authors have written extensively on the calculation of density from composition, often with intention to support some hypothesis as to the constitution of glass. Among these are Biltz and Weibke[2] and Knapp.[3]

Units and Factors

Density is expressed in terms of the mass of unit volume, and its dimensions are M/V, or ML^{-3}. The temperature to which the measurement refers should be specified. Density requires no reference to other substances, and when such a reference is given, *e. g.*, $d^{25°}_{4°}$, the property probably meant is specific gravity, the ratio between the mass of unit volume of the substance at a particular temperature divided by the mass of unit volume of water at 4°, a dimensionless quantity. The two measures are not the same, and should not be confused.

Methods of Measurement

Four methods are commonly used for measuring density: the volumetric method, the flotation method, the method of Archimedes, and the pyknometric method.

The volumetric method, in which the volume is calculated from the dimensions of the sample, is frequently useful for rough approximations; but the precision of geometrical form necessary for exact work is difficult to attain.

The method of Archimedes, or the displacement method, in which the sample is weighed both in air and immersed in a liquid of known density, is rapid and convenient, and sometimes is capable of high precision. It is necessary that there be careful control of the density of the buoyant liquid, which should not be too viscous; and the error caused by surface tension acting on the suspension wire as it passes through the air-liquid interface must be eliminated as far as possible. The method is frequently applied at ordinary temperature, using water as the buoyant liquid, and a fine platinum wire, previously coated with platinum black, for the suspension, under which conditions acceptable precision can be attained. The density at high temperature is sometimes measured by the buoyant effect of the glass on a platinum weight; but under these conditions the viscosity of the liquid, and the effects of the suspension wire passing through the interface, cause the method to

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[2] Biltz, W., and Weibke, F., *Z. anorg. allgem. Chem.*, **203**, 345 (1932).

[3] Knapp, O., *Sprechsaal*, **63**, 61 (1930); *Glastech. Ber.*, **8**, 154 (1930).

be of questionable value. Another application of the same principle was made by Day, Sosman, and Hostetter[4] in their study of mineral densities at high temperatures, in which a bath of molten tin was used as the buoyant liquid. The method gives excellent results with rigid materials, but with glasses which flow under load, disturbing complications arise.

The pyknometric method, in which a container is weighed first filled with a liquid of known density, then filled with a known weight of glass immersed in the liquid, is standard practice, yet the precision of which the method is capable is rarely attained. Certain precautions are essential. The fragments of glass always tend to entrap bubbles of air, and tiny cracks, invisible except when filled with a colored liquid, contain air which is difficult to displace. The complete removal of air can be assured only by boiling under reduced pressure, as was done by Day and Allen[5] and by Johnston and Adams,[6] who also described a superior pyknometer.

The flotation method, in which the density of a buoyant liquid is adjusted so that the density of the sample is exactly matched, is especially well known to mineralogists. It offers many advantages. It is capable of the highest precision, and some of the most precise determinations of density have been made by it. It is also of special value in detecting inhomogeneity, and in the rapid measurement of a number of samples not differing greatly in density. The method has been applied to glass by Cousen and Turner[7] and by Morey and Merwin.[8]

Determinations of density which lay claim to highest accuracy should be corrected for the buoyant effect of the air. This may be done by making separate corrections on each weight, but it is much easier, and less liable to error, to make the correction for buoyancy in one operation, as was done by Johnston and Adams. They showed that if s is the density of a substance as calculated from the uncorrected weights, S its true density, and L the true density of the liquid, then the vacuum correction to be applied to the uncorrected density x is $0.0012\ (1 - s/L)$; when the density of the substance is greater than that of the liquid, the correction is negative. Using water as the buoyant liquid, the correction is -0.0012 for a solid of density 2, and -0.0024 for one of density 3.

Several studies which are not quoted in detail have included measurements of the density of experimental glasses. Gehlhoff and Thomas[9] measured numerous glasses, which were not analyzed, and gave their

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[4] Day, A. L., Sosman, R. B., and Hostetter, J. C., *Am. J. Sci.*, **37**, 1 (1914).

[5] Day, A. L., and Allen, E. T., *Carnegie Inst. Wash. Pub.* No. 31 (1905).

[6] Johnston, J., and Adams, L. H., *J. Am. Chem. Soc.*, **34**, 563 (1912).

[7] Cousen, A., and Turner, W. E. S., *J. Chem. Soc.*, **1928**, 2654.

[8] Morey, G. W., and Merwin, H. E., *J. Optical Soc. Am.*, **22**, 632 (1932).

[9] Gehlhoff, G., and Thomas, M., *Z. tech. Physik*, **7**, 105 (1926).

results in graphic form only. Enss[10] gave the density of numerous glasses measured incidentally in studying chemical durability, but included no details of measurement. Hänlein[11] measured the density, coefficient of expansion, viscosity and electrical conductivity of a number of glasses in the system Na_2O-K_2O-CaO-SiO_2. His results are given only in graphic form, on too small a scale to be reproduced. Keppeler and Ippach[12] in their study of chemical durability in the system Na_2O-CaO-SiO_2 determined the density of 20 analyzed glasses, which contained about one per cent of impurity, some of which were strongly colored from iron. The results are not included because they are inferior to other measurements in the same composition range which are given in detail.

Densities of glasses not included in the discussion in this chapter are in Tables VII. 8, I. 2, VIII. 2, XVI. 22, and XVI. 23.

One-Component Glasses

Elementary glasses. Selenium is the only element whose density as a glass has been measured. Saunders,[13] in a study of the forms of selenium, found the density of selenium glass to be 4.28.

Oxide Glasses

Boric oxide, B_2O_3. The density of boric oxide has been measured by several observers, some of whom have exercised great care; nevertheless, the effect of heat treatment, and the procedure necessary to dehydrate the oxide completely appear not to have been studied adequately. Small amounts of water increase the density of boric oxide until a maximum is reached,[14] and the glass is extraordinarily susceptible to heat treatment.

Ditte[15] found the density of B_2O_3 was 1.8766 at 0°, 1.8476 at 12°, and 1.6988 at 80°. Bedson and Williams[16] found a density of 1.850. Briscoe, Robinson, and Stephenson[17] found that the density ranged from 1.7911 to 1.7904, with a mean value of 1.7952. Cousen and Turner[18] criticised the results of Briscoe, Robinson, and Stephenson on the basis that the heat treatment given the boric oxide was not sufficient to dehydrate it, and that there was no proper annealing. They made a careful study of these factors, and give 1.844 as the true density of boric oxide. Both pyknometer and flotation methods were used. In a later

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[10] Enss, J., *Glastech. Ber.*, **5**, 449 and 509 (1928).

[11] Hänlein, W., *Z. tech. Physik*, **14**, 418 (1933).

[12] Keppeler, G., and Ippach, H., *Sprechsaal*, **60**, 239, 261, 281, and 297 (1927).

[13] Saunders, A. P., *J. Phys. Chem.*, **4**, 423 (1900).

[14] Unpublished results of Merwin, H. E., and Morey, G. W.

[15] Ditte, A., *Ann. chim. phys.* (5), **13**, 67 (1878).

[16] Bedson, P. P., and Williams, C., *Ber.*, **14B**, 2549 (1881).

[17] Briscoe, H. V. A., Robinson, P. L., and Stephenson, G. E., *J. Chem. Soc.*, **1926**, 70.

[18] Cousen, A., and Turner, W. E. S., *J. Chem. Soc.*, **1928**, 2654.

paper[19] this value was abandoned, and the value 1.8391 was given without discussion. Jenckel[20] found 1.8016 for the density at 20° of a quenched sample.

By the flotation method Wulff and Majumdar[21] obtained values of the density of B_2O_3 ranging from 1.778 to 1.838, depending on the history of the sample. The highest density was obtained with a sample incompletely dehydrated by heating one hour at 800° followed by slow cooling. They believed that complete dehydration would require heating in vacuum at 1200°. They also found that the "annealing" treatment * greatly influenced the density. A sample heated 24 hours in a high vacuum at 100-120° C., then melted for 24 hours in a high vacuum at 1200° C. and quickly cooled, gave 1.778. Another sample, similarly heated, but cooled in 8 hours, gave 1.811; and another, cooled in 13 hours, gave the most probable value of the density of boric oxide, 1.812. They were of the opinion that the results of Turner and his collaborators were too high owing to incomplete dehydration.

TABLE X. 2—Density and Refractive Index of Some Na_2O-B_2O_3 Glasses
After Jenckel (J) *and Wulff and Majumdar* (WM)

Weight % Na_2O	Density	n_D	Observer
5.42	2.0716	1.49003	J
6.84 *c*	1.9690	1.4797	WM
6.84 *d*	1.9876	1.4841	WM
9.15	2.0090	1.4839	WM
9.91	2.1728	1.49623	J
10.81	2.1881	1.50011	J
14.13	2.2489	1.50425	J
16.97	2.2878	1.50802	J
16.51 *a*	2.1226	1.4953	WM
16.51 *b*	2.1235	1.4958	WM
20.51	2.1376	1.50962	J
23.19	2.2303	1.5051	WM
23.55	2.3363	1.51026	J
27.19	2.3524	1.51130	J
28.28	2.3285	1.5136	WM
28.41 *a*	2.3322	1.5144	WM
28.41 *b*	2.3324	1.5147	WM
30.79	2.3622	1.51290	J

Values indicated by *a* and *b* were made on different portions of the same piece; *c* refers to a quickly cooled sample, *d*, to one slowly cooled.

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[19] Gooding, E. J., and Turner, W. E. S., *J. Soc. Glass Tech.*, **18**, 32 (1934).

[20] Jenckel, E., *Z. Elektrochem.*, **41**, 211 (1935).

[21] Wulff, P., and Majumdar, S. K., *Z. physik. Chem.*, **31B**, 319 (1936).

* The annealing treatment affecting density is mainly that in the temperature range immediately below that at which strain is rapidly lost. As the viscosity increases the time required to reach the final density at that temperature increases; and to obtain the maximum density the rate of cooling should be such as to permit the maximum change at each temperature. Such a treatment has never been given boric oxide glass. The statement "cooled in 8 hours" means nothing; the important part of the cooling may have taken only one-half hour.

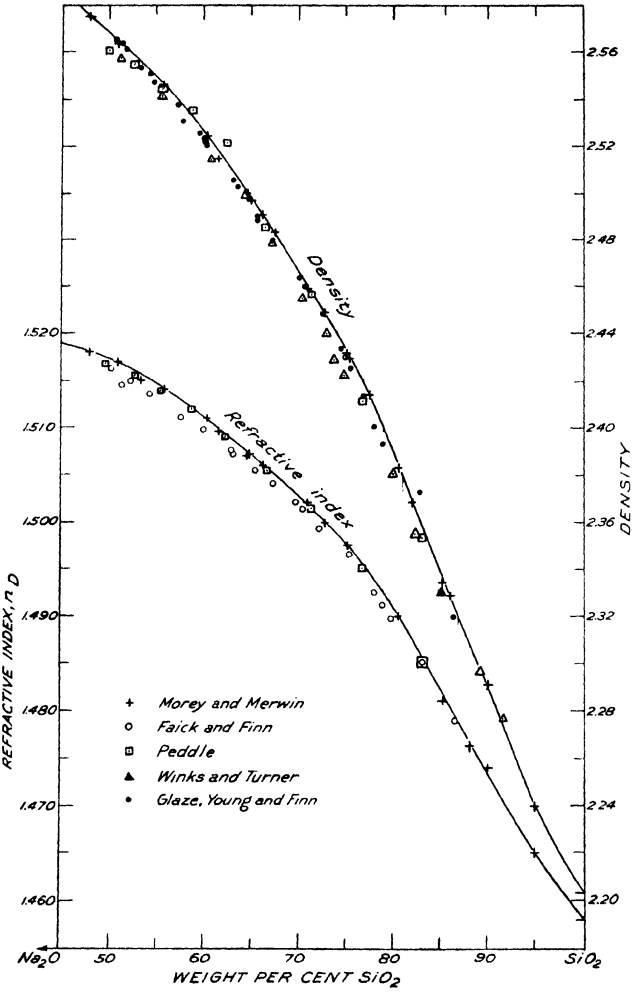

FIGURE X. 1.—The Densities and Refractive Indices of Glasses in the System Na_2O-SiO_2, as Determined by Several Observers. After Morey and Merwin.

Silicon Dioxide, Silica or Quartz Glass, SiO_2. The literature concerning the density of silica glass has been critically discussed by Sosman,[22] who concluded that the most probable value of the density of vitreous silica at 0° C. and one atmosphere is 2.203.

Germanium Dioxide, GeO_2. Dennis and Laubengayer [23] found 3.6277

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[22] Sosman, R. B., "The Properties of Silica," 289, Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

[23] Dennis, L. M., and Laubengayer, A. W., *J. Phys. Chem.*, 30, 1510 (1926).

TABLE X. 3—Compositions, Densities, and Coefficients of Expansion of Some Glasses Studied at the Department of Glass Technology, University of Sheffield, Sheffield, England

No.	SiO_2	B_2O_3	Na_2O	CaO	MgO	K_2O	Al_2O_3	Fe_2O_3	TiO_2	ZrO_2	PbO	BaO	FeO	ZnO	Density	$\alpha \times 10^8$
System[1] Na_2O-CaO-SiO_2																
1	74.05		25.34	0.21	tr.		0.24	0.14							2.4353	1153
600*	79.84		19.46	0.12	tr.		0.69	0.11							2.3748	
2	73.92		23.80	1.50	tr.		0.20	0.14							2.4384	1106
3	74.08		23.00	2.61	tr.		0.21	0.15							2.4416	1065
4	74.07		21.50	3.81	tr.		0.28	0.14							2.4462	1021
5	73.78		20.87	4.50	0.15		0.38	0.19							2.4507	988
673*	73.18		19.38	6.26	0.21		0.58	0.61							2.4602	
7	74.41		17.20	7.45	0.24		0.30	0.40							2.4650	911
8	74.99		16.00	8.16	0.26		0.31	0.09							2.4682	870
9	74.94		14.88	9.36	0.28		0.42	0.16							2.4757	844
10	74.59		14.22	10.38	0.30		0.45	0.21							2.4840	810
11	74.93		13.02	11.68	0.31		0.38	0.17							2.4904	769
16[b]	66.71		12.72	18.17	0.85		1.41	0.31							2.5866	882
17[b]	69.73		11.22	17.38	0.55		0.50	0.25							2.5547	801
* Lit. ref. 6.																
System[2] Na_2O-MgO-SiO_2																
24	74.07		24.23	*a*	1.10		0.37	*a*							2.4323	104
25	74.35		23.46	*a*	1.85		0.75	*a*							2.4300	1069
26	75.00		22.12	*a*	2.49		0.26	*a*							2.4273	1005
27	75.16		20.69	*a*	3.47		0.46	*a*							2.4239	947
28	75.19		19.83	*a*	4.20		0.52	*a*							2.4207	895
329	76.30		18.26	*a*	5.09		0.74	*a*							2.4149	841
330	77.09		16.05	*a*	6.10		0.68	*a*							2.4102	784
331	76.68		15.77	*a*	6.87		0.93	*a*							2.4055	754
332	76.86		14.55	*a*	7.46		0.93	*a*							2.4032	710
389	77.77		13.40	*a*	8.45		0.56	*a*							2.3967	645
390	78.28		11.76	*a*	9.30		0.91	*a*							2.3947	594
System[3] Na_2O-MgO-CaO-SiO_2																
490	74.76		14.84	7.52	1.64		0.93	0.08							2.4637	781
491	74.74		14.98	6.43	2.58		1.02	0.06							2.4569	779
492	75.58		14.48	5.48	3.66		0.87	0.07							2.4496	775
493	76.32		14.58	3.82	4.10		0.87	0.07							2.4364	746
494	76.00		14.98	3.14	4.85		0.90	0.08							2.4265	739
System Na_2O-Al_2O_3-SiO_2																
441A*	74.30		22.68	0.08	tr.		2.72	0.07							2.4294	1088
442*	73.30		22.20	0.02	tr.		4.25	0.02							2.4247	1020
443D*	72.05		20.62	0.12	tr.		6.85	0.12							2.4181	939
444B*	72.19		18.79	0.08	tr.		8.96	0.08							2.4103[c]	811
445D*	72.27		16.61	0.21	tr.		10.71	0.07								764
446C*	71.56		15.28	0.21	tr.		12.69	0.10							2.4010	710

680†	75.12		18.22	0.16	tr.	6.46	0.08			2.4022	854
682†	70.76		18.56	0.09	tr.	10.49	0.09			2.4198	877
683†	62.25		17.95	0.06	tr.	19.69	0.10			2.4309	862
684†	79.21		14.26	0.10	tr.	6.53	0.09			2.4493	729
684A†	74.72		14.71	0.10	tr.	10.64	0.05			2.3646	723
685†	69.99		14.43	0.09	tr.	15.50	0.07			2.4015	727
458	73.98	13.54	7.10	tr.		7.10	0.10				688
459	74.25	12.72	7.91	0.06		5.23	0.07				700
460	74.13	13.54	9.74	0.09		2.67	0.09				736

* Lit. ref. 4. † Lit. ref. 5.

a CaO and Fe_2O_3 are included under Al_2O_3.

b 16 and 17 contain 0.30 and 0.47% As_2O_3, resp.

c In a later paper (5) 2.4099 and 858 are given for *d* and α.

System[9] *Na_2O-TiO_2-SiO_2*

753a	74.58		22.36	0.04		0.95	0.11	2.04		2.4355	
753b	75.22		20.71	tr.		0.89	0.10	3.01		2.4380	
753c	76.30		18.06	0.16		0.87	0.19	4.52		2.4465	
753d	74.96		17.32	0.12		0.52	0.12	6.88		2.4661	
753e	73.56		16.40	0.58		1.15	0.15	8.06		2.4672	
753f	73.00		15.14	0.81		1.06	0.19	9.89		2.4833	
754a	73.42		23.68	0.12		0.53	0.13	1.94			1035
754b	72.88		23.16	0.18		0.44	0.15	3.01			990
754c	72.82		21.82	0.16		0.29	0.10	4.95			903
754d	73.30		18.78	0.26		0.61	0.11	6.88			874
754f	72.61		16.31	0.07		0.65	0.16	10.03			807
754k	72.41		11.90	0.06		0.75	0.15	14.91			619
754n	70.52		8.24	0.06		1.84	0.17	19.45			

System[10] *Na_2O-ZrO_2-SiO_2*

748a	73.77		24.70	0.07		0.47	0.08	tr.	0.95	2.4397	1106
748b	74.14		22.60	0.05		0.67	0.07	tr.	2.67	2.4563	1028
748c	72.80		22.15	0.05		1.33	0.08	0.09	3.54	2.4655	1006
748d	72.88		20.69	0.04		1.45	0.07	0.13	4.67	2.4780	961
748e	72.96		20.12	0.05		1.36	0.09	0.15	5.39	2.4884	935
748f	71.89		19.32	0.06		1.74	0.08	0.15	6.97	2.5045	885
748g	71.97		18.90	0.06		0.82	0.09	0.18	8.25	2.5206	844
748h	72.10		16.89	0.06		0.70	0.09	0.21	10.33	2.5046	808
757b	71.01		22.45	0.22		0.77	0.08	0.11	5.35	2.4963	1015
757c	65.59		21.40	0.23		1.20	0.09	0.23	11.13	2.5852	935
757d	61.10		21.75	0.17		1.42	0.09	0.29	15.15	2.6698	910
757/2	56.38		21.09	0.17		1.21	0.08	0.37	20.59	2.7527	859
797a	75.00		18.74			0.41	0.05	0.12	5.80	2.4624	871
797b/2	69.32		18.42			0.49	0.05	0.19	11.73	2.5554	801
797c	65.08		18.78			0.98	0.06	0.22	14.80	2.6264	845
803a/2	72.77		20.42	tr.	3.24	0.93	0.05	tr.		2.4494	939
803b	72.42		18.50	tr.	4.96	2.27	0.09	0.07	1.83	2.4532	871
803c	73.15		18.40	tr.	3.46	1.21	0.07	0.10	3.74	2.4705	863
803d	72.36		19.11	tr.	1.83	0.45	0.05	0.12	5.95	2.4835	849
803e	71.34		18.82	tr.	0.23	1.36	0.06	0.17	8.01	2.5073	848

TABLE X. 3—(*Continued*)

No.	SiO_2	B_2O_3	Na_2O	CaO	MgO	K_2O	Al_2O_3	Fe_2O_3	TiO_2	ZrO_2	PbO	BaO	FeO	ZnO	Density	$\alpha \times 10^8$
796a	76.31		19.71	tr.	3.24		0.76	0.05							2.4203	911
796b	74.58		20.00	tr.	2.56		0.62	0.05	d	2.24					2.4524	910
796c/2	72.98		21.04	tr.	1.76		0.71	0.05	d	3.35					2.4755	903
System[11] Na_2O-PbO-SiO_2																
804a	72.86		22.62				0.48	0.08			3.75				2.5045	1090
804b	70.97		20.49				0.44	0.08			7.89				2.5840	1041
804c	67.78		18.65				0.46	0.08			12.56				2.6360	997
804d	65.84		17.73				0.43	0.07			15.70				2.7246	964
804e	64.55		15.55				0.42	0.10			19.11				2.8105	928
804f	62.44		15.35				0.34	0.06			22.31				2.8845	903
804g	60.88		14.00				0.42	0.06			24.46				2.9267	870
804h	59.34		12.31				0.42	0.06			27.77				2.9960	842
System[7] B_2O_3-SiO_2																
816a	6.46	93.54													1.8599	
816b	9.99	90.01													1.8682	
816c	14.81	85.19													1.8838	
816d	24.45	75.55													1.9135	
816e	38.03	61.97													1.9608	
816f	45.51	54.49													1.9865	
816g	52.17	47.83													2.0031	
816h	57.24	43.76													2.0224	
System[6] Na_2O-B_2O_3-SiO_2																
601	74.22	4.46	19.78	0.14	tr.		0.93	0.14							2.4291	840
602	71.56	8.28	18.76	0.10	tr.		1.00	0.08							2.4710	817
603	68.39	11.29	18.92	0.12	tr.		1.01	0.09							2.4919	813
604	64.72	14.45	19.95	0.14	tr.		0.72	0.06							2.5055	837
605	61.28	18.84	18.93	0.11	tr.		0.74	0.08							2.5126	805
606	50.04	28.83	20.36	0.08	tr.		0.78	0.05							2.4890	814
607	35.22	39.99	23.71	0.16	tr.		0.84	0.07							2.4526	
608	32.23	43.70	23.08	0.22	tr.		0.84	0.07							2.4262	
609	70.75	18.71	9.79	0.10	tr.		0.82	0.07							2.3449	498
610	74.91	12.45	11.26	0.10	tr.		0.89	0.05							2.4173	578
611	67.18	21.81	10.13	0.13	tr.		0.88	0.07							2.3215	497
612	61.94	25.82	11.19	0.14	tr.		0.84	0.11							2.2862	521
613	57.87	31.26	9.55	0.09	tr.		0.98	0.08							2.2672	542
614	52.11	36.17	10.34	0.10	tr.		0.89	0.11							2.2269	557
615	46.30	42.33	10.44	0.08	tr.		0.80	0.10							2.2020	570
616	41.29	46.07	11.49	0.13			0.80	0.10							2.2072	606
System[8] Na_2O-K_2O-CaO-B_2O_3-SiO_2																
755	75.82	....	6.86	8.56		7.90	0.59	0.07							2.4649	802
755B	75.38	0.66	6.84	8.52		8.02	0.44	0.08							2.4651	795
755D	75.38	2.05	6.14	8.40		9.38	0.65	0.07							2.4841	785

d A small amount of TiO_2 is included in ZrO_2.

755E	69.06	5.44	7.54	8.64	8.22	0.91	0.08			2.5173	746
755F	68.20	7.90	7.00	8.70	7.56	0.65	0.09			2.5185	734
755G	66.50	9.58	7.04	8.72	7.40	0.65	0.09			2.5256	714
755H	64.58	10.78	7.50	8.60	7.42	0.91	0.09			2.5254	701
755J	62.42	13.65	6.26	8.90	8.06	0.62	0.08			2.5285	693
755K	56.76	19.43	7.38	8.54	7.14	0.90	0.10			2.5230	695
755L	53.26	22.54	6.74	9.10	6.98	1.17	0.11			2.5215	694
755M	49.50	25.70	7.00	9.08	7.50	0.80	0.08			2.5127	700
755N	46.66	29.57	5.36	8.62	8.06	1.59	0.15			2.4867	
755O	41.98	33.79	6.52	8.56	7.38	1.65	0.15			2.4721	739
755P	36.94	40.12	7.00	8.82	4.22	2.24	0.19			2.3936	

System[16] Na_2O-SiO_2

128	91.60		8.4							2.2677	
127	88.17		11.83							2.2967	
126	85.04		14.86							2.3298	
125	82.34		17.66							2.3559	
124	79.93		20.07							2.3802	
123	77.30		22.70							2.4017	
122	74.65		25.35							2.4230	
121	73.59		26.41							2.4287	
120	72.80		27.20							2.4401	
119	70.27		29.73							2.4556	
118	67.11		32.89							2.4785	
117A	64.34		35.66							2.4941	
116A	60.71		39.29							2.5153	
115	55.42		44.58							2.5418	
114	51.15		48.85							2.5568	

System[12] Na_2O-BaO-SiO_2

798a	72.86		23.30			0.65	0.06	3.03		2.4795	1102
798b	71.46		21.95			0.62	0.06	5.98		2.5182	1068
798c	70.83		20.11			0.55	0.06	8.59		2.5705	1048
798d	68.72		19.49			0.51	0.06	11.07		2.6057	1034
798e	68.33		17.39			0.38	0.05	14.16		2.6537	1001
798f/2	66.33		15.89			0.52	0.06	17.28		2.7146	950
798g	64.94		14.98			0.87	0.07	19.38		2.7622	956
798i	62.67		11.72			1.23	0.06	24.25		2.8577	884
798h/2	63.18		12.52			1.84	0.08	22.37		2.8127	888
798j	59.97		11.20			2.39	0.08	26.15		2.8841	

System[13] Na_2O-FeO-Fe_2O_3-SiO_2

814a	72.18		23.80	0.20		0.41	2.21		0.63	2.4807	1050
814b	71.33		21.36	0.06		0.58	4.84		0.84	2.5145	990
814c	69.02		22.36	0.06		0.70	6.52		1.05	2.5404	999
814d	70.00		17.38	0.10		0.80	9.95		1.05	2.5457	862
814e	69.25		17.20	0.05		1.01	10.16		1.89	2.5653	833
814f	66.63		15.34	0.06		0.66	15.42		1.78	2.5798	
814g	65.64		14.46	tr.		0.42	15.03		4.20	2.5992	
814h	63.72		13.66	0.06		0.97	17.19		3.88	2.6202	
814i	63.69		11.54	0.03		0.86	20.50		3.36	2.6330	
814j	62.97		10.64	0.03		0.52	21.90		3.99	2.6442	

TABLE X. 3—*(Continued)*

System[14] *Na_2O-ZnO-SiO_2*

No.	SiO_2	B_2O_3	Na_2O	CaO	MgO	K_2O	Al_2O_3	Fe_2O_3	TiO_2	ZrO_2	PbO	BaO	FeO	ZnO	Density	$\alpha \times 10^8$
788a	74.09		24.07	0.05			0.68	0.04						1.29	2.4520	1081
788b	73.48		21.89	0.06			0.77	0.07						3.51	2.4675	1016
788c	73.52		20.63	0.06			0.88	0.09						4.55	2.4817	959
788d	73.36		19.48	0.04			0.88	0.06						6.12	2.5050	917
788e	75.06		17.07	0.05			0.88	0.06						6.70	2.4869	842
788f/2	72.11		17.20	0.08			0.89	0.04						9.54	2.5247	875
788g/2	72.46		15.40	0.06			0.60	0.06						11.13	2.5428	779
788h/2	71.94		14.70	0.06			1.76	0.09						11.39	2.5499	
788i	73.26		12.73	0.04			0.67	0.04						13.07		
788j	72.01		11.80	0.05			0.53	0.09						15.22		

System Na_2O-B_2O_3-SiO_2

Series Na_2O-B_2O_3

No.	SiO_2	B_2O_3	Na_2O	Density
26B		96.56	3.38	1.8632
26C		97.66	2.36	1.8662
25B		92.18	7.78	1.9367
6B		88.56	11.43	2.0631
35		86.28	13.76	2.1285
5B		84.22	15.80	2.1639
34		78.19	21.76	2.2486
4C		81.47	18.46	2.2309
1H		69.88	30.18	2.3703

Series Na_2-SiO_3-B_2O_3

No.	SiO_2	B_2O_3	Na_2O	Density
14A	50.01	8.89	40.80	
14B	49.00	7.63	43.29	2.5435
22B	45.52	14.86	39.27	2.5394
27A	40.64	21.59	37.33	2.5373
28A	34.67	31.29	34.24	2.5327
22C	53.24	21.36	25.48	2.5453
28C	51.61	25.11	23.38	2.5407
28B	43.20	36.05	20.59	
29C	33.44	41.92	24.50	2.4872
29A	25.72	48.89	25.47	
29B	35.38	55.51	9.16	
30A	19.18	57.01	23.64	2.3315
31B	20.50	57.33	22.38	
31	22.54	63.73	13.82	
32C	13.22	70.24	16.75	2.1830
32	11.57	81.43	7.13	

System[17] *Li_2O-Na_2O-CaO-SiO_2*

No.	SiO_2	Na_2O	K_2O	CaO	Li_2O	RbO	Density
164	74.84	0		10.10	15*		2.4539
165	74.94	2		9.94	13		2.4559
166	74.96	4		10.08	11		2.4630
167	75.02	6		10.00	9		2.4665
168	75.14	9		9.93	6		2.4748
169	74.96	11		10.02	4		2.4836
170	75.10	13		9.91	2		2.4840
171	75.00	14		10.25	1		2.4821
172	75.08	14.75		10.22	0		2.4816

* In these glasses, SiO_2 and CaO were determined by analysis; Na_2O and Li_2O are the batch compositions.

System[17] *Li_2O-K_2O-CaO-SiO_2*

No.	SiO_2	Na_2O	K_2O	CaO	Li_2O	RbO	Density
173	75.04		3	10.02	12†		2.4490
174	75.09		6	9.95	9		2.4437
175	75.18		9	9.90	6		2.4422
176	75.06		11	9.91	4		2.4412
177	75.02		13.5	9.99	1.5		2.4385
178	75.04		14	9.93	1		2.4374
179	75.04		14.5	10.07	0.5		2.4358
180	74.92		14.95	10.04	0		2.4365

† In these glasses, SiO_2 and CaO were determined by analysis; K_2O and Li_2O are the batch compositions.

System[17] *Na_2O-K_2O-CaO-SiO_2*

No.	SiO_2	Na_2O	K_2O	CaO	Li_2O	RbO	Density
181	75.07	12.94	1.94	9.98			2.4772
182	75.02	11.06	4.12	9.87			2.4733

15D	3.01	89.80	7.25	1.8721
33	4.44	89.99	5.35	1.9060
15E	2.86	95.00	1.95	
15B	2.42	94.84	2.77	

Series $NaBO_2$-SiO_2

40	20.95	42.32	37.62	2.4728
41	30.83	34.76	34.32	2.5140
39	42.58	31.28	26.32	2.5306
37	52.94	26.65	20.63	2.5326
36	66.05	16.80	16.98	2.4911
38	74.56	14.50	11.34	2.4401
42	80.00	9.74	9.10	2.3701

183	75.04	8.97	6.11	10.03		2.4673
184	74.97	5.98	9.00	10.00		2.4599
185	74.86	4.13	11.17	10.07		2.4537
186	75.15	1.85	13.04	10.13		2.4423

System[17] K_2O-Rb_2O-CaO-SiO_2

187	74.78		13	10.09	2‡	2.4483
188	74.87		10	10.14	5	2.4700
189	75.09		7	10.00	8	2.4902
190	75.13		4	10.08	11	2.5085
191	74.89		0	10.01	15	2.5388

‡ In these glasses, SiO_2 and CaO were determined by analysis; K_2O and Rb_2O are batch compositions.

1. English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **4**, 126 (1920).
2. English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **4**, 153 (1920).
3. English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **6**, 228 (1922).
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10. Dimbleby, V., English, S., Firth, E. M., Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **11**, 52 (1927).
11. English, S., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **11**, 300 (1927).
12. English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **11**, 425 (1927).
13. English, S., Howes, H. W., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **12**, 31 (1928).
14. English, S., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **12**, 287 (1928).
15. Gooding, E. J., and Turner, W. E. S., *J. Soc. Glass Tech.*, **18**, 32 (1934).
16. Winks, F., and Turner, W. E. S., *J. Soc. Glass Tech.*, **15**, 185 (1931).
17. Waterton, S. C., and Turner, W. E. S, *J. Soc. Glass Tech.*, **18**, 268 (1934).

for the density of glassy GeO_2 at 20°. The pyknometric method was used, with toluene as liquid, but no information was given as to the thermal history of the sample.

Arsenic Trioxide, As_2O_3. Merwin[24] found the density of quickly cooled As_2O_3 glass to be 3.701.

Two-Component Glasses

Na_2O-B_2O_3. Gooding and Turner[25] studied glasses in this system, with the results given in Table X. 3. Details of their method are described under the system Na_2O-B_2O_3-SiO_2.

Jenckel[20] used the flotation method in measuring some glasses which had been chilled. Wulff and Majumdar[21] also used quickly cooled glasses, with the exception of one glass both chilled and slowly cooled. The results of these observers are combined in Table X. 2. The agreement is not good, which is not surprising when it is considered that the annealing treatment, of great importance in these glasses, was not the same.

Na_2O-SiO_2. The studies of the density of glasses in the binary system Na_2O-SiO_2 considered in this section were made at ordinary temperatures; the results of a study of density at high temperatures are in the last section of this chapter (p. 259). Peddle[26] made an extensive study of a number of systems, determining density and optical properties. Density was determined by the method of Archimedes, using water, except with silicates affected by it, in which cases toluene was used. His work was primarily exploratory, and great accuracy was not claimed. Compositions were calculated from the quantities of the components melted, and accordingly they are in error by unknown and variable amounts. His results are assembled in Table XVI. 9, and are included in Fig. X. 1.

The results of Winks and Turner,[27] obtained by the flotation method, are given in Table X. 3, and shown in Fig. X. 1. The glasses were "carefully annealed"; and from other experiments from the same laboratory, it is inferred that the heat treatment was in the upper part of the annealing range.

The results of Glaze, Young, and Finn[28] are included in Fig. X. 1 and are given in Table X. 4, together with the annealing temperatures. They considered their results were best represented by three straight lines (cf. p. 250).

The results of Morey and Merwin[1] are in Table XVI. 11 and Fig. X. 1. They attempted to anneal their glasses in such a manner as to

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[24] Merwin, H. E., private communication.

[25] Gooding, E. J., and Turner, W. E. S., *J. Soc. Glass Tech.*, **18**, 32 (1934).

[26] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 3 (1920).

[27] Winks, F., and Turner, W. E. S., *J. Soc. Glass Tech.*, **15**, 185 (1931).

[28] Glaze, F. W., Young, J. C., and Finn, A. N., *Bur. Standards J. Research*, **9**, 799 (1932).

TABLE X. 4—Composition and Properties of Some Glasses Studied at the Bureau of Standards, Washington, D. C.*

No.	Composition			Density 20°	n_D	Annealing temp. (° C.)	Expansion 25°-400°	Critical temp. (° C.)	Expansion 25° to critical temp. (° C.)	Softening temp. (° C.)	Expansion 25° to softening temp. (° C.)
	SiO_2	CaO	Na_2O								
1	50.04		49.96		1.5163	415					
2	50.22		49.78	2.5656		450					
3	50.51		49.49	2.5640		450					
4	51.26		48.74		1.5146	420					
5	51.61		48.39	2.5607		440					
6	52.15		47.85		1.5150	420	81			440	95
7	52.60		47.40	2.5537		460					
8	53.62		46.38	2.5515		450					
9	54.14		45.86	2.4575	1.5137	420	76	426	84	450	94
10	56.56		43.44	2.5383		450					
11	57.45		42.55	2.5318	1.5112	430	73	428	81	460	89
12	58.98		41.02	2.5266		460					
13	59.69		40.31	2.5240		450					
14	59.71		40.29	2.5228		470					
15	59.97		40.03	2.5208	1.5099	430	70	442	80	460	85
16	62.77		37.23	2.5071		470					
17	62.86		37.14	2.5044	1.5076	440	66	445	76	470	82
18	63.06		36.94	2.5038	1.5075	440					
19	65.30		35.70	2.4890	1.5055	450	61	457	73	490	80
20	65.32		34.68	2.4924	1.5055	480					
21	66.52		33.48	2.4865		480					
22	67.14		32.86	2.4807	1.5042	500	58	460	69	490	77
23	69.65		30.35	2.4644	1.5021	515	55	470	67	505	76
24	70.21		23.79	2.4612	1.5014	525	55	470	68	500	77
25	70.44		29.56	2.4603	1.5015	525	55	467	68	500	77
26	72.15		27.85	2.4488	1.4993	525	51	473	64	500	72
27	72.33		27.67	2.4479		500					
28	74.16		25.84	2.4343		505					
29	74.69		25.31	2.4305		505					
30	75.29		24.71	2.4260	1.4695	560					
31	76.60		23.40	2.4140		510	44	480	56	510	63
32	76.65		23.35	2.4133		510	44	485	58	510	65
33	76.70		23.30	2.4126		550					
34	77.85		22.15	2.4007	1.4925	575	41	486	53	525	63
35	78.61		21.39	2.3935	1.4912	575	40	490	53	520	60
36	79.73		20.27	2.3813	1.4898	575	38	489	50	530	57
37	80.04		19.96				38	492	50	525	55
38	82.72		17.28				34	495	45	540	53
39	82.76		17.24	2.3545		550	34	500	45	550	52
40	82.86		17.14	2.3536	1.4851	600					
41	85.15		14.85	2.3307		540					
42	86.41		13.59	2.3204	1.4790	600					
43	50.18	12.02	37.80	2.6413		460					
44	50.30	6.66	43.04	2.6076		450					
45	52.20	19.83	27.97				59	498	80	535	90
46	54.37	12.78	32.85	2.6236	1.5391	530	62	477	79	505	83
47	56.20	9.80	34.00	2.5976	1.5320	480	67	470	84	495	90
48	56.34	19.75	23.91				51	517	73	550	80
49	56.76	5.76	34.48	2.5719	1.5238	470	67	444	77	480	87
50	58.41	3.05	38.54	2.5474	1.5170	480	68	437	77	473	88
51	60.05	20.16	19.79				49	548	74	580	81

* The measurements of density of the soda-lime-silica glasses are by Glaze, Young and Finn; of refractive index, by Faick and Finn; and of expansion, by Schmid, Finn and Young. All the measurements on the soda-alumina-silica glasses are by Faick, Young, Hubbard and Finn.

TABLE X. 4.—(*Continued*)

No.	Composition			Density 20°	n_D	Annealing temp.(°C.)	Expansion 25°-400°	Critical temp.(°C.)	Expansion 25° to critical temp.(°C.)	Softening temp.(°C.)	Expansion 25° to softening temp.(°C.)
	SiO_2	CaO	Na_2O								
52	60.32	15.18	24.50	2.6074	1.5395	530	52	520	74	547	79
53	62.93	19.68	17.39				43	568	69	595	77
54	63.34	12.27	24.39	2.5757	1.5320	525	52	518	74	550	81
55	64.14	14.64	21.22	2.5851	1.5360	565	47	530	69	570	76
56	64.70	8.46	26.84	2.5460	1.5232	525	52	493	71	530	81
57	65.71	5.50	28.79	2.5229	1.5167	520	53	493	72	515	79
58	66.05	16.03	17.92				44	563	69	595	78
59	66.12	19.91	13.97				40	587	67	625	77
60	66.47	11.79	21.74	2.5564	1.5288	565	48	522	72	560	84
61	67.23	21.15	11.62				37	601	64	645	75
62	67.30	3.27	29.43	2.4998	1.5110	520	53	480	69	515	78
63	67.98	9.52	22.50	2.5331	1.5230	565	47	518	68	560	82
64	70.12	14.85	15.03				39	567	63	610	73
65	70.50	6.50	23.00	2.4980	1.5145	530	45	506	62	545	73
66	71.70	16.20	12.10				35	598	60	630	65
67	72.08	13.71	14.21	2.5276	1.5265	580	36	571	59	615	68
68	72.61	3.15	24.24	2.4641	1.5060	525	46	490	61	530	72
69	74.09	10.68	15.23	2.4935	1.5182	545	36	555	57	600	68
70	74.69	13.03	12.28	2.4961	1.5211	590	33	589	57	627	66
71	75.48	9.26	15.26	2.4734	1.5135	590	36	553	54	600	65
72	78.56	2.99	18.45				38	504	52	545	60
73	78.77	4.90	16.33	2.4190	1.5003	545	34	523	51	565	61
74	80.59	3.24	16.17	2.3886	1.4935	565	32	505	43	560	55
				System Na_2O-Al_2O_3-SiO_2							
		Al_2O_3									
101	50.32	2.86	46.82	2.5605	1.5162						
102	50.57	7.00	42.43	2.5495	1.5164			447	82	489	94.5
103	50.86	6.71	42.43	2.5484	1.5155			447	83.7	492	98.5
104	50.89	9.57	39.54	2.5410	1.5150			455	82.0	501	99.0
105	50.95	4.88	44.17	2.5533	1.5157			435	84.2	472	94.8
106	55.25	9.83	34.92	2.5182	1.5116			477	76.0	517	86.2
107	55.56	6.94	37.50	2.5259	1.5120			457	77.2	501	90.5
108	55.66	9.68	34.66	2.5163	1.5110						
109	55.80	4.83	39.23	2.5304	1.5124			440	79.0	484	91.5
110	55.86	4.83	39.23	2.5304	1.5124			445	78.9	492	93.0
111	60.45	9.84	29.71	2.4897	1.5072						
112	60.68	4.86	34.46	2.5032	1.5088			465	74	504	86.2
113	60.76	2.82	36.42	2.5111	1.5092			455	75.4	491	86.0
114	60.78	1.09	38.13	2.5168	1.5094						
115	60.88	9.59	29.53	2.4891	1.5070			495	68.8	530	79.4
116	60.97	6.57	32.46	2.4977	1.5073						
117	64.78	1.02	34.20	2.4916	1.5059			458	72.2	500	84.5
118	65.10	9.96	24.94	2.4615	1.5032			510	65.2	561	76.8
119	65.70	4.75	29.55	2.4749	1.5049			475	70.4	530	84.6
120	65.88	9.43	24.69	2.4580	1.5025			505	62	550	72.0
121	65.90	2.87	31.23	2.4830	1.5052			470	72	500	85.2
122	65.92	2.41	31.67	2.4814	1.5047						
123	66.36	2.03	31.61	2.4805	1.5050			470	67.2	517	83.0
124	67.42	4.45	28.34	2.4653	1.5026						
125	67.75	2.95	29.30	2.4683	1.5030						
126	68.10	6.75	25.15	2.4539	1.5018			493	63	540	74.2
127	68.78	5.77	25.45	2.4534	1.5006						
128	69.99	0.97	29.04	2.4612	1.5020			470	69.6	515	81.5
129	70.11	2.03	27.86	2.4572	1.5015			476	65.1	520	76.5

TABLE X. 4.—(*Continued*)

No	Composition SiO₂	Composition Al₂O₃	Composition Na₂O	Density 20°	n_D	Annealing temp. (°C.)	Expansion 25°-400°	Critical temp. (° C.)	Expansion 25° to critical temp. (° C.)	Softening temp. (°C.)	Expansion 25° to softening temp. (° C.)
130	70.30	4.86	24.84	2.4445	1.5003			490	60.3	535	70.4
131	70.63	4.92	24.45	2.4428	1.5000			490	61.0	541	76.9
132	70.84	2.85	26.31	2.4509	1.5007						
133	70.88	6.49	22.63	2.4343	1.4988			500	57.7	553	69.5
134	71.08	9.32	19.60	2.4214	1.4970			522	54.0	570	67.5
135	73.15	0.98	25.87	2.4396	1.4984						
136	73.81	4.69	21.50	2.4181	1.4957			502	53.0	552	64.0
137	74.75	0.98	24.27	2.4277	1.4970						
138	74.88	3.00	22.12	2.4162	1.4955						
139	74.95	1.07	23.98	2.4234	1.4960			481	60.2	531	74.8
140	74.98	2.00	23.02	2.4186	1.4952			490	57.7	539	66.0
141	75.21	5.12	19.67	2.4025	1.4934			502	48.2	550	54.8
142	75.48	4.82	19.70	2.4022	1.4935						
143	75.61	2.85	21.54	2.4022	1.4949			495	54.5	539	66.0
144	77.71	0.93	21.36	2.4013	1.4926						

attain the highest density, and their densities are above those of the other observers. The systematic differences in the four sets of observations are all within the amount which may be caused by differences in heat treatment.

K_2O-SiO_2. The only measurements of density in this system are those of Merwin and Morey, given in Table XVI. 17. The data of Peddle, included in Table XVI. 9, represent values extrapolated from the ternary system K_2O-CaO-SiO_2.

TABLE X. 5.—Density of Lead Oxide-Silica Glasses.

(*After Weiller*)

Wt. pct. PbO	Density	Wt. pct. PbO	Density
91.8	8.06	75.91	5.74
91.4	8.12	72.44	5.28
87.0	7.005	71.0	5.20
84.0	6.94	67.66	4.87
82.2	6.45	66.22	4.74
79.62	6.14		

CaO-SiO_2. Larsen[29] gave the density of CaO-SiO_2 glasses as 2.904. Several glasses in this binary system measured by Morey and Merwin, are included in Table XVI. 11, and as end-members of Fig. X. 5.

SrO-SiO_2 and BaO-SiO_2. Eskola[30] determined the densities of a few glasses in this system, using the pyknometric method, with the results given in Table XVI. 8. The density given for SrO-SiO_2 glass was quoted by Eskola from Jaeger and van Klooster.[31]

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[29] Larsen, E. S., *Am. J. Sci.*, **28**, 263 (1909).

[30] Eskola, P., *Am. J. Sci.*, **4**, 331 (1922).

[31] Jaeger, F. M., and van Klooster, H. S., *Proc. Acad. Sci. Amsterdam*, **6**, 896 (1916).

B_2O_3-SiO_2. The densities of a few glasses in this system, measured by Cousen and Turner,[32] are included in Table X. 3. Merwin and Morey measured three glasses, with the results given in Table XVI. 5.

PbO-SiO_2. The densities of these glasses, measured by Weiller,[33] are given in Table X. 5. The densities of lead-silica glasses containing small amounts of alkali oxide, measured by Andersen and Merwin, are in Table XVI. 7.

Three-Component Glasses

Na_2O-BeO-SiO_2. Lai and Silverman [34] measured the density of some glasses in this system, using the method of Archimedes with water as the buoyant liquid. The results, together with batch compositions, are given in Table X. 6. The density increased with the content of BeO,

TABLE X. 6—Density and Refractive Index of Some Glasses Containing Beryllium Oxide

After Lai and Silverman

No.	Molecular Ratios				Density	Refractive Index
	Na_2O	K_2O	BeO	SiO_2		
			System Na_2O-BeO-SiO_2			
A1	1		0.50	4.25	2.4168	1.4975
A2	1		0.75	4.25	2.4322	1.5025
A3	1		1.00	4.25	2.4436	1.5078
A4	1		1.25	4.25	2.4556	1.5121
B1	1		0.50	4.00	2.4266	1.5010
B2	1		0.75	4.00	2.4396	1.5054
B3	1		1.00	4.00	2.4499	1.5096
B4	1		1.25	4.00	2.4613	1.5126
C1	1		0.50	3.75	2.4385	1.5018
C2	1		0.75	3.75	2.4548	1.5073
C3	1		1.00	3.75	2.4667	1.5108
C4	1		1.25	3.75	2.4780	1.5149
D1	1		0.50	3.50	2.4491	1.5036
D2	1		0.75	3.50	2.4637	1.5086
D3	1		1.00	3.50	2.4787	1.5120
D4	1		1.25	3.50	2.4885	1.5172
			System K_2O-BeO-SiO_2			
E4		1	1.25	3.00	2.4827	1.5183
E5		1	1.50	3.00	2.4775	1.5201
E6		1	1.75	3.00	2.4727	1.5216
F4		1	1.25	3.25	2.4760	1.5170
F5		1	1.50	3.25	2.4717	1.5184
F6		1	1.75	3.25	2.4675	1.5197
G4		1	1.25	3.50	2.4683	1.5152
G5		1	1.50	3.50	2.4630	1.5173
G6		1	1.75	3.50	2.4578	1.5187
H4		1	1.25	3.75	2.4639	1.5146
H5		1	1.50	3.75	2.4594	1.5152
H6		1	1.75	3.75	2.4554	1.5163

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[32] Cousen, A., and Turner, W. E. S., *J. Soc. Glass Tech.*, **12**, 169 (1928).

[33] Weiller, P., *Sprechsaal*, **43**, 726 (1910).

[34] Lai, C. F., and Silverman, A., *J. Am. Ceram. Soc.*, **11**, 535 (1928).

but was less than the density of glasses of similar molecular composition containing MgO or CaO in place of BeO.

Becker[35] studied three series of glasses (Table X. 7). In the *A* series, to a parent glass made to have the composition $Na_2O \cdot 3SiO_2$, (but actually containing SiO_2, 73.60%; Na_2O, 25.01%; CaO, 0.37%; Al_2O_3, 0.69%; Fe_2O_3, 0.06%), he added BeO in steps of 0.2 mole up to 1.8 moles. In the *P* series, the glasses had the composition $(1 - x)$ Na_2O, xBeO, $3SiO_2$; and in the *V* series 0.25 and 0.50 moles of BeO, MgO, CaO, or Al_2O_3 were added to the parent glass. The densities were measured by the displacement, the pyknometric and the flotation methods. Those given in Table X. 7 were measured by the displacement method and the accuracy was given as plus or minus two in the third decimal place.

TABLE X. 7—Properties of Some Glasses Containing Beryllium Oxide

After C. A. Becker

No.	Mole Per cent BeO	n_C	n_D	n_F	Density	$\alpha \times 10^8$	Trans-formation Point	Annealing Temp.
A 1	0.00	1.4957	1.4983	1.6043	2.434	1134	425	475
2	4.78	1.5019	1.5045	1.5106	2.462	1078	435	514
3	8.96	1.5082	1.5106	1.5168	2.485	1034	490	544
4	12.75	1.5135	1.5161	1.5225	2.505	995	520	573
5	16.61	1.5182	1.5209	1.5268	2.520	990	545	597
6	19.99	1.5226	1.5250	1.5312	2.531	1002	565	614
7	22.69	1.5264	1.5291	1.5353	2.541	960	575	630
8	25.83	1.5285	1.5312	1.5374	2.542	939	590	643
9	28.25	1.5316	1.5341	1.5404	2.550	939	595	650
10	30.95	1.5336	1.5364	1.5425	2.548	911	600	655
P 2	2.79	1.4966	1.4991	1.5052	2.432	1017	445	493
3	5.08	1.4975	1.4999	1.5063	2.428	901	475	579
4	8.09	1.4990	1.5016	1.5072	2.428	814	505	563
5	10.25	1.5002	1.5026	1.5081	2.427	783	535	594
V 2	5.75	1.5036	1.5062	1.5122	2.467	1043	470	522
3	11.52	1.5114	1.5142	1.5201	2.497	1009	510	559
	MgO							
4	5.79	1.5015	1.5040	1.5102	2.461	1047	435	448
5	11.28	1.5057	1.5082	1.5147	2.479	1042	450	501
	CaO							
6	5.96	1.5118	1.5145	1.5209	2.496	1061	455	508
7	11.91	1.5244	1.5270	1.5337	2.556	1074	480	535
	Al_2O_3							
8	6.09	1.4986	1.5011	1.5071	2.444	957	465	521
9	11.47	1.4989	1.5015	1.5073	2.444	832	525	582

Na_2O-MgO-SiO_2. Measurements in this system by English and Turner[36] on a series (24-28, 329-390) of trisilicate glasses are given in Table X. 3, and Fig. X. 2. Peddle[37] measured some glasses of the gen-

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[35] Becker, C. A., *Sprechsaal,* **67**, 137, 152, 169, 185, 203, 216, 233, 250 (1934).

[36] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **4**, 153 (1920).

[37] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 281 (1920).

eral formula $5SiO_2 \cdot (2 - x)\ Na_2O \cdot xMgO$, with the results given in Table XVI. 9 (series 200). The batch compositions only were given, and there were no details as to method.

Na_2O-CaO-SiO_2. The most complete studies of density at ordinary temperature have been made in this system by Peddle, by English and Turner, by Glaze, Young, and Finn, and by Morey and Merwin. The range of compositions studied by each of these is indicated in Fig. X. 3. Some measurements of density at high temperature are mentioned on p. 259.

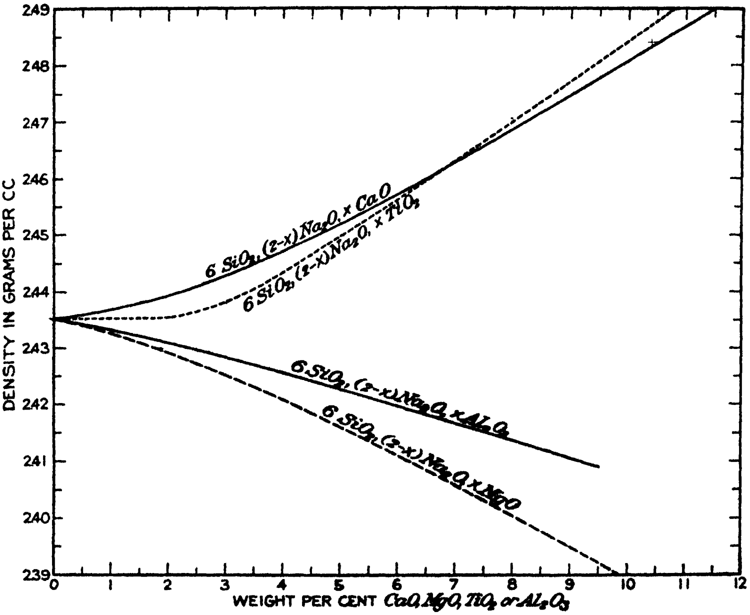

FIGURE X. 2.—Densities of Some Glasses of the Formula $(2 - x)\ Na_2O + x[MgO, CaO, Al_2O_3 \text{ or } TiO_2] + 6SiO_2$. After Turner and Associates.

Morey and Merwin [1] made a study of the effect of heat treatment on density. The compositions studied are indicated by the several fields of Fig. X. 4, and the detailed results are in Table X. 8 A, B, and C. Some of their discussion follows:

> "It was desired to make our measurements on glasses reproducible and comparable, free from the influence of such variables as might be introduced by heat treatment. It has long been believed that mechanical strain appreciably affects the optical properties and density of glass,[38] and that the effects can be removed by heat treatment,

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[38] Hovestadt, H., "Jena Glass," translated by Everett, J. D. and A., Macmillan, New York, 1902.

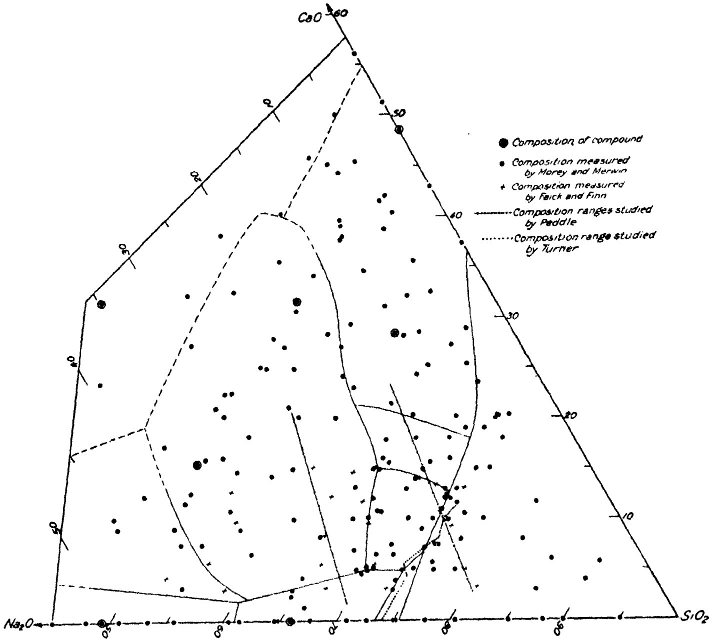

FIGURE X. 3.—The Compositions of Glasses in the System Na_2O-CaO-SiO_2 studied by Different Observers. After Morey and Merwin.

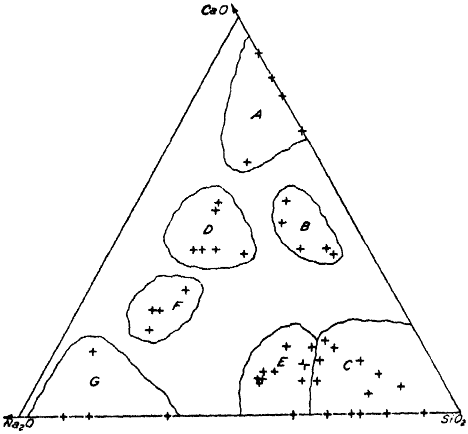

FIGURE X. 4.—Compositions of Glasses Used by Morey and Merwin in Studying the Effect of Heat Treatment on Density.

but it is not evident in what manner a system of balanced stresses such as exist in strained glass could affect the bulk density or refractive index. Whether or not the effect of heat treatment consisted solely in the removal of mechanical strain seemed an open question, but the results obtained by several investigators[39] have made it seem probable that the effect is not only to remove the mechanical strain, but also to produce other definite changes in the glass. Our experiments have led to similar conclusions. It was found that over wide ranges of composition, density changes produced by heating over night

TABLE X. 8A—Effect of Different Heat Treatments on Glasses in the Ternary System Na_2O-CaO-SiO_2. Density Changes* Near the Softening Temperature

After Morey and Merwin

Glass Nos. and area, Fig. X. 4		600°		650°		700°	760°	800°	830°	875°	915°	450° to 500°
		15 m.	45 m.	15 m.	17 hrs. (3 hrs.)	15 m.	5 m.	15 m.	10 m.	5 m.	5 m.	17 hrs.
152	*A*		+2							*n*	*n*, *d*	+ 6
139				+ 8								+ 6
125				+ 1	+6		+2	0	0	0, *n*	*n*, *d*	+ 5
107				+ 2	+9[1]		0, *r*					+ 3
124			+5	+ 4	(+4)		−2		−7	*n*†	*n*, *d*	+ 3
97	*B*		+3	+ 1	(+2)		−2, *r*					+ 6
82				<+11								+16
63				+11								+12
50*a*		+5	+6 [+9][4]			−1	*n*	−4, *r*†				+ 3
9	*C*			+ 1		−2		−2, *r*				+ 6
5				<+ 4								+ 7
8				0		0, *r*						+ 6
4				− 7								+ 2
127	*D*			*d*								+13
104		0		*n*		−4, *r*						+ 4
119			0									+ 6
126*a*			+1	*d*								<+ 5
58	*E*	−3, *n*		−3, *r*[3]								+ 7
47				+10								+16
60				−4, *r*								+ 3
122*a*	*F*		0	*d*								+ 2
131			*d*[2]									<+ 5
146	*G*		*d*									+ 3

* Differences (heat treated − original) × 10^3.

d, devitrified or decidedly opalescent; *n*, no evidence of surface flowage; *r*, corners rounded or surface showing polish due to slight flowage; † slight opalescence; < samples which before this heating had a maximal density (as indicated by the figures), are less dense after heating.

[1] Density increased 0.006 in 3 hours.

[2] Also was devitrified after 7 days at 383°.

[3] Rounding visible after 5 minutes.

[4] Density was 0.009 higher after 21 hours at 600°, but a similar heating did not change the density of a piece which had previously acquired a high density.

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[39] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **4**, 153 (1920). Tool, A. Q., and Eichlin, C. D., *J. Optical Soc. Am.*, **8**, 419 (1924). Tool, A. Q., and Eichlin, C. D., *J. Am. Ceram. Soc.*, **8**, 1 (1925). Tool, A. Q., and Hill, E. E., *J. Soc. Glass Tech.*, **9**, 185 (1925). Peters, C. G., *Bur. Standards Scientific Papers*, **521**, (1926)

at 450° to 500° were about equal. As work progressed, other heat treatments were found to give greater changes, especially in glasses of extreme composition. In some early tests the amount of surface volatilization was determined by careful weighings, but in no case was the amount significant.

"The compositions studied most thoroughly are shown in Fig. [X. 4], and are given in Table [XVI. 11], and the density changes are given in Table [X. 8 A, B, C]. For these experiments pieces weighing about 0.3 g. were used. Table [X. 8A] gives the results of heatings of 5 to 15 minutes at increasing temperatures, made to determine where the glasses begin to show "fire polish," by incipient flowage at the surface, or where they begin to crystallize without such flowage. These samples were cooled rapidly by dropping from the furnace into the air. The densities after heating at the highest temperatures were the lowest, often 0.004 to 0.007 less than for samples prepared as already described. Glasses of area *A*, Fig. [X. 4], with over 40 per cent CaO and little Na_2O, gave these low densities when cooled from about 900°, at which temperature they crystallized without definite surface flowage. Glasses of area *G*, containing 40 per cent or more of Na_2O and little CaO, devitrify or show surface flowage after a few minutes heating at about 500°. Many compositions near the side CaO-SiO_2, and containing more than 75 per cent SiO_2 cannot be made into homogeneous glasses because of formation of immiscible liquids, or of crystallization, or of the presence of fine bubbles. The highest silica glasses in areas *B* and *C* showed evidence of surface flowage at 800° in 15 minutes, and when quenched were 0.002 to 0.004 less dense than the original glasses. Beyond the area *ADFG* the glasses crystallize so readily that no studies of minimum density could be carried out.

"As to maximal density, a general, but not in all cases detailed, agreement was found. The detailed results of these studies are assembled in Tables [X. 8B] and [X. 8C]. At about 200° to 300° below the temperature of incipient flowage a glass may be brought to a maximal density within the relatively short time of a few hours or days. From this temperature to that of incipient flowage the ultimate density diminishes regardless of the time of heating; somewhat below this temperature maximal density may be reached with long-continued heating. The lime-silica glasses in area *A* required several hours at 600° to 650° to complete this density change, which amounted to from 0.004 to 0.009. The total density differences between maximal and minimal values were 0.006 to 0.011. In area *B* the maximal density was attained at 460° to 600°, and the total changes were 0.013 to 0.016. In area *C* the temperatures were about as in *B* but the total changes were only 0.008-9. In area *D* and *E* the minimal

TABLE X. 8B—Effect of Different Heat Treatments on Glasses in the Ternary System Na_2O-CaO-SiO_2. Density Changes* in the Annealing Ranges.

Glass Nos.	and area, Fig. X. 4	555°			500°			460°				383° or (400°)				325°		277°	230°
		15 m.	3 hrs.	24 hrs.	1 hr.	17 hrs.	41 hrs.	2 hrs. or 6 hrs.	17 hrs.	38 hrs.	3½ da.	6 hrs.	2 da.	3½ da.	7 da.	2 da.	123 da.	22 da.	109 da.
139	A		+ 6						+ 6								+ 9[a]		
98	B	+12							+11										
82		+12	+14						+16[f]								+11[a]		
63		+ 7	+ 9						+12[f]								+11[a]		
50a		+ 3		+9	+4	+9	+9	+2	+ 3	+4	+ 5	(+1)	(+1)	(+ 2)	(+ 2)				
5	C[1]	+ 3	+ 6						+ 7										
127	D	+ 4	+11						+13								+10		(0)[c]
104		+ 1		+5	+4	+7	+7	+2	+ 4	+5	+ 5	(+1)	(+1)	(+ 2)	(+ 4)				
126a								(+5)	+ 6						+ 6	+ 5			
131a								(+5)	+ 7						+ 8	+ 7			
48	E								+ 7					+ 6	+ 8	0			+ 1
58		— 1		—3	+5	+5	+5	+6	+ 7	+8	+10	(+4)	(+5)	+(6)	(+ 6)[e]				
57									+ 6					+ 8	+ 9				
47		+11	+11						+16							+ 3	+15		
53									+ 6					+10	+10				
122a	F								+ 2					+ 4	+ 4				
133									+18					+15		+ 6			+ 3
134a								(+2)	+ 5						+11	+ 5			
131								(+5)						+13	devit.	+ 7			
146	G								+ 3				+7		+ 8				
98a								[+11][h]				[+10][g]				+16		+15[d]	+14[b]

[a] Density at 650° remained unchanged.
[b] Increased 10 in 47 days at 230°.
[c] Refers to No. 131c having similar composition.
[d] Changed 13 in 3 days.
[e] A piece which had gained 10 at 460° did not change, but an unannealed piece gained 6.
* Differences (heat treated − original) × 10^3.

[f] Temperature 450°-500°.
[g] 16 hours at 375°.
[h] 15 hours at 460°.
[1] See Table X. 8A.

densities were found near 600°, the maximal near 400°, and the total change was about 0.015. Especially near areas *F* and *G*, glasses may tend to become opalescent, owing to devitrification, in the temperature range in which several days heating is required to obtain maximal density (see No. 131, Table [XVI. 11]). In some cases the opalescence is so slight that it can be detected only by scattered light, when the pieces of glass are immersed in liquid of about the same refractive index. Sometimes it is not possible to separate the change in density resulting from such slight devitrification from the change in glass density which is under consideration; although more frequently a different order of magnitude in the rate of change in density makes it possible to avoid confusion.

TABLE X. 8C—Effect of Different Heat Treatments on Glasses in the Ternary System Na_2O-CaO-SiO_2. Density Changes* at 395°

Glass Nos. and area, Fig. X. 4		Days at 395°				
		2	6	12	21	29
1	*C*	2				
1*a*		3[a]	5	5		
2*a*		4[a]	5	5		
3*x*[b]		9	9			
3*a*		2	3	3		
3*b*		5	5			
5*a*		7	8	9	10	
9*b*		7	9	9		
10			0	2	2	
11		5	6	6		
13	*E*	8	9	10	11	11
17		4	5	8	8	
20		3[a]	5	7	8	8
21		7	0	0		

[a] Gain in 15 hrs. at 460°.

[b] A 0.3-gram charge in a tight platinum container quenched from 1450° in mercury, $d = 2.320$. A similar charge cooled in air, $d = 2.333$. A 5-gram charge cooled on a metal plate, $d = 2.320$–2.335 for small fragments. Both of the last looked clear, but when suspended in a heavy liquid and illuminated from the side milkiness appeared. The crystals were not visible with the microscope.

* Differences (heat treated − original) × 10^3.

"Several of the harder glasses were heated to give maximal density in a few hours at 500-550°, and then heated for about 4 months at 230°, or for 3 months at 330°. They did not change. Samples of the same or similar glasses which were low in density increased in density, but did not quite reach the maximal value.

"Glasses that reach a maximal density in a few hours at 500° to 550° may require more than a week to reach a higher maximum at 400°.

"The observed total density differences have not exceeded 0.018, except for No. 68a, in which the difference was 0.024, and for glasses highest in lime the change has been about 0.008 and still less for those

> very high in silica. Most of the change has been an increase over the original density."[40]
>
> "The annealing procedure adopted fulfilled our object of making measurements on glasses in a reproducible condition, but whether or not the glasses were exactly comparable is an open question. We have no generally accepted explanation of what takes place in glass during annealing, in addition to the removal of mechanical strain; and not until we have some knowledge of the processes taking place can we select a heat treatment which will give us glasses in a corresponding state, if such a term has any meaning. It might be argued that it would be better to anneal each glass at its 'annealing temperature,' by which is meant an experimentally obtained temperature dependent upon composition, dimensions, time and rate of cooling, to which commercial glasses are subjected in order to bring about desirable changes. The temperature so determined is an arbitrarily selected point of the viscosity-temperature curve, and there is no reason to assume that the process whose progress is measured by the change in density or refractive index would come to a definite conclusion at a definite viscosity. In our opinion, the heat treatment we have selected, designed to bring out a maximal density or refractive index, gives more nearly comparable data than would have been obtained at the 'annealing temperature.'"

The results of Morey and Merwin are in complete harmony with later knowledge of the effect of heat treatment on the properties of glass, given in the chapters on viscosity and annealing.* The properties of glass, including the density, are affected by heat treatment in the "annealing range," and for each temperature there is an equilibrium condition. Above the annealing range the equilibrium condition is reached quickly, and to obtain the glass in a condition characteristic of a temperature well above the annealing range requires exceedingly rapid chilling. Within the annealing range the glass takes on the equilibrium or stabilized condition more slowly, the more slowly the lower the temperature; and if the stabilized condition is not reached, the density measured will be that of some higher temperature, not that of the temperature of heat treatment.

> "The final results on the density of the glasses are assembled in Table [XVI. 11], and presented graphically in Fig. [X. 5]. In Table [XVI. 11] the glasses are arranged in order of decreasing SiO_2 content and the compositions are given in the second, third, and fourth columns; values enclosed in parentheses were obtained by difference.

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[40] Differences of 0.004 in density of different parts of No. 9a, which was very rapidly cooled, disappeared on annealing. Usually differences as large as this could be related to chemical inhomogeneity.

* See pp. 142 and 181.

These compositions are plotted in Fig. [X. 5]. Column 5 gives the observed density at 20° of the annealed glasses, and column 6 gives the corrections to add to the observed values to fit the smoothed curves of Fig. [X. 5]. In most cases determinations were made on both unannealed and annealed glasses, and column 7 gives the experimentally determined increase in density on annealing. Some glasses

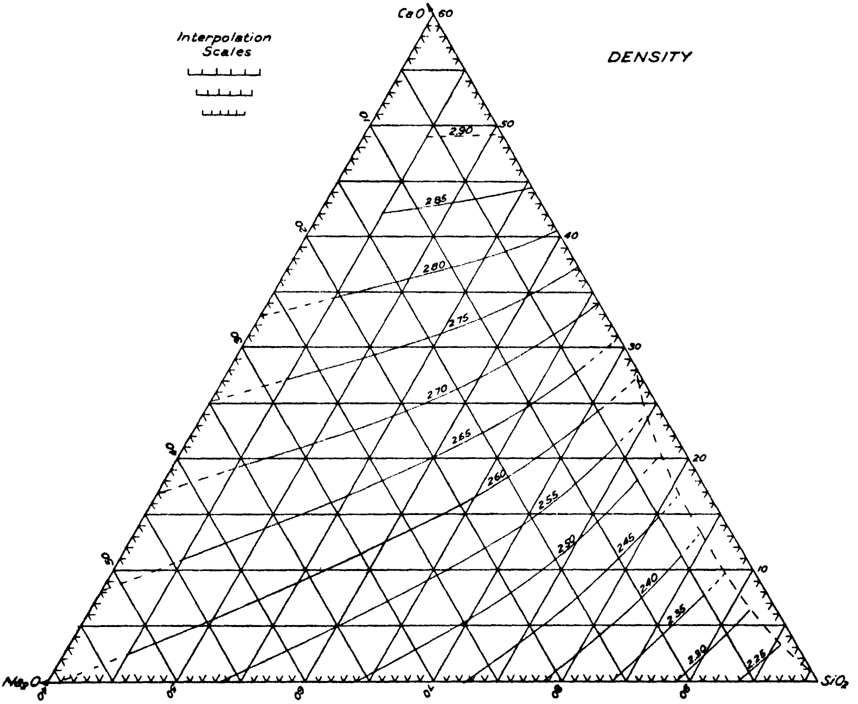

FIGURE X. 5.—Relation between Density and Composition in the System Na_2O-CaO-SiO_2. After Morey and Merwin.

were not successfully annealed, usually because of devitrification, and in such cases an estimated difference, indicated by parentheses in column 7, was added to the density of the unannealed glass."

Peddle's results[41] (Table XVI. 9) refer to two series of glasses of the general formula $100SiO_2 + 40$ (or 20) $Na_2O + x$ moles CaO (series 163 and 165); and hence represent addition of CaO to the glasses $100SiO_2 + 40$ (or 20) Na_2O. Some measurements were made on glasses in which SiO_2 was held constant at 70, 65, or 60 per cent, while the proportions of Na_2O and CaO were altered (Series 171). All compositions were cal-

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[41] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 20 (1920).

culated from the batches melted, supplemented by four analyses showing the significant amounts of impurities introduced by attack on the clay pot in which they were melted. The method of annealing was not given.

The compositions of the glasses measured by English and Turner,[42] given in Table X. 3, and shown in Fig. X. 2, were determined by analysis. They were made to be of "trisilicate" composition, by molecular replacement of Na_2O by CaO in the glass $Na_2O \cdot 3SiO_2$. Density was measured by the pyknometric method on annealed particles graded between 10- and 30-mesh screens. The results of these observers do not differ from those of Morey and Merwin by amounts greater than is to be expected from the differences in heat treatment.

The systems of planning composition variations used by Peddle and by Turner and his co-workers are not greatly different, in that both are methods of defining straight lines in a ternary diagram. The system used by Peddle (addition of the variant oxide, holding constant the ratio of SiO_2 to Na_2O, *e. g.*, $100SiO_2 + 40Na_2O + x\text{CaO}$) defines a straight line from the point on the side Na_2O-SiO_2 to the CaO-apex; that used by Turner (substitution of the variant oxide for Na_2O in a glass of the composition $Na_2O + 3SiO_2$) defines a straight line for the composition of the trisilicate of sodium to that of the variant oxide. Many other systems may be suggested; and endless variations can be obtained by the use of molecular percentages, using either the oxides themselves or any desired combination of oxides. Any such scheme, however, merely serves to define a straight line; and any straight line so defined will remain a straight line when the system of coördinates is changed from percentages by weight to percentages by moles. Much of the argument between advocates of the several systems is pointless. All such arbitrary excursions into a ternary system of necessity give a distorted and incomplete picture of the relationships in the system as a whole, and are not a substitute for systematic exploration of the entire field.

The results of Glaze, Young, and Finn [28] are given in Table X. 4, and include the annealing temperatures used by them. They believed that their results were best represented by families of straight lines, having different constants as the proportion of SiO_2 was increased. The general formula used by them was

$$1/D = \alpha A + \beta B + \gamma C + \gamma' C^2$$

in which *A*, *B*, and *C* represent the percentages by weight of SiO_2, Na_2O, and CaO, respectively. The values of the constants α, β, etc., and the limits of the percentages of SiO_2 within which each of these sets of constants is applicable, are given in Table X. 9.

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[42] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, 4, 126 (1920).

Morey and Merwin, who measured a larger range of composition, found no justification for representing the densities by straight lines. Their experiments "included so many data that they might be expected to indicate whether or not the iso-curves should be continuously curved or segmented into two or three less curved lines. No evidence of such segmentation was found. However, each might be replaced by three 'best' straight lines without producing departures greater than the departures of single observations, but the distribution of departures would be too highly systematic to be tolerated." The lines of constant density are curved, but the curvature is slight.

TABLE X. 9—Silica Limits and Values of the Corresponding Constants for the Equations Used by Glaze, Young and Finn for Calculation of Density in the System Na_2O-CaO-SiO_2

Silica limits, weight per cent SiO_2	$\alpha\ 10^3$	$\beta\ 10^3$	$\gamma\ 10^8$	$\gamma'\ 10^6$
50(?) to A_a	4.252	3.537	2.545	8.0
A_a to A_b	4.3028	3.4628	2.500	4.0
A_b to A_c	4.3922	3.2872	2.285	5.0
A_c to 100	4.5400	2.8460	1.844	14.8

$A_a = 59.4 - 0.23\ (\%\ CaO) + 0.032\ (\%\ CaO)^2$.
$A_b = 66.3 + 0.15\ (\%\ CaO) - 0.004\ (\%\ CaO)^2$.
$A_c = 74.9 - 0.017\ (\%\ CaO)^2$.

Na_2O-ZnO-SiO_2. This system was studied by English, Turner, and Winks.[43] The glasses were made according to the formula $6SiO_2\ (2 - x)\ Na_2O$, xZnO, and thus belonged to the large series of trisilicate glasses studied by English and Turner and their co-workers. The compositions and densities are given in Table X. 3.

Na_2O-BaO-SiO_2. This system was studied by Peddle[44] and by English and Turner.[45] Peddle studied the two series of glasses $100SiO_2 + 40$ (or 20) $Na_2O + x$BaO (series 190 and 191), and also a series (196) in which SiO_2 was held constant at 70, 65, 60, or 50 per cent, and the ratio of BaO to Na_2O was altered. The results are given in Table XVI. 9, and shown in Fig. X. 6. English and Turner replaced Na_2O by BaO in the trisilicate glass $Na_2O + 3SiO_2$, with the results given in Table X. 3. The two groups of observations are not directly comparable, since the two composition ranges are not the same.

Na_2O-B_2O_3-SiO_2.. English and Turner[46] studied two series of glasses in this system, made according to the formulas, by weight: $20Na_2O$, $(80 - x)\ SiO_2$, xB_2O_3; and $10Na_2O$, $(90 - x)\ SiO_2$, xB_2O_3. The compositions and densities are recorded in Table X. 3. In the series containing

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[43] English, S., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, 12, 287 (1928).

[44] Peddle, J. C., *J. Soc. Glass Tech.*, 5, 201 and 228 (1921).

[45] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, 11, 425 (1927).

[46] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, 7, 73 and 155 (1923).

20 per cent Na_2O, the density rose to a maximum, and in the series with 10 per cent Na_2O, the density fell to a minimum.

Gooding and Turner[47] made a more extensive study of glasses in the binary systems Na_2O-B_2O_3 (up to the composition $Na_2O \cdot 2B_2O_3$), Na_2SiO_3-B_2O_3, and $NaBO_2$-SiO_2. The compositions and densities are given in Table X. 3. They used the flotation method on glasses pulverized to 10- to 30-mesh and washed with alcohol to remove dust. The glasses were annealed by heating to the annealing temperature as determined by an optical method, cooling at 0.5° to 1° per minute for the first 100°, then in a freely cooling furnace. The density curve for the system $NaBO_2$-SiO_2 showed a flat maximum. The system Na_2O-B_2O_3 showed a rapid diminution in density as the Na_2O content increased; and the system Na_2SiO_3-B_2O_3 showed first a flat portion, in which addition of B_2O_3 had little effect, then a rapid diminution in density.

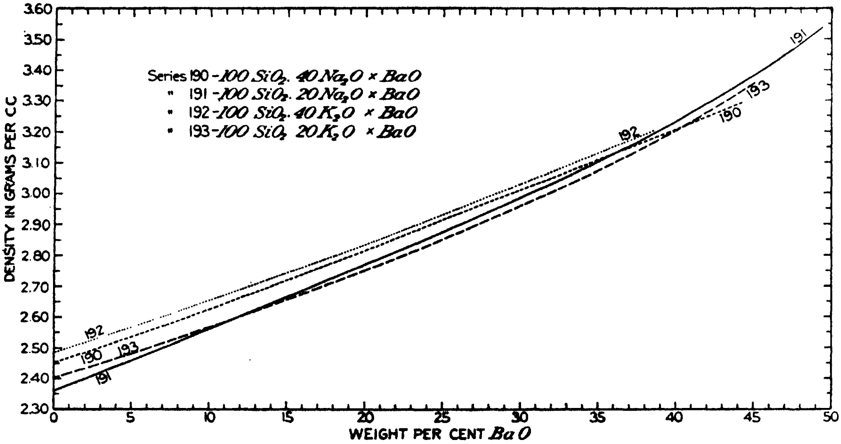

Figure X. 6.—Densities of Some Glasses in the Systems Na_2O-BaO-SiO_2 and K_2O-BaO-SiO_2 of the Approximate Compositions Shown. After Peddle.

Numerous as are the measurements on glasses containing Na_2O, B_2O_3, and SiO_2, they are not sufficiently accurate to map out a consistent picture of the relation between composition and density in the ternary system. Mixtures approaching $NaBO_2$ in composition cannot be obtained as glass, and mixtures rich in B_2O_3 show unusually large effects of heat treatment in the annealing region. When a complete study is made, it is probable that the lines of constant density will not be simple.

Na_2O-Al_2O_3-SiO_2. Measurements in this system were made by Eng-

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[47] Gooding, E. J., and Turner, W. E. S., *J. Soc. Glass Tech.*, **18**, 32 (1934).

lish and Turner,[48] by Dimbleby, English, Hodkin, and Turner,[49] and by Faick, Young, Hubbard, and Finn.[50] The measurements by Turner and his collaborators, which are included in Table X. 3, were made by the pyknometric method, using grains graded between 10- and 30-mesh screens. The study by English and Turner (series 441-6) was of trisilicate glasses in which the Na_2O in the composition $Na_2O + 3SiO_2$ was replaced in molecular proportions by Al_2O_3, and it was found that such replacement diminished the density (Fig. X. 2). In the second study (series 680-85), by Dimbleby, English, Hodkin, and Turner, it was planned to hold Na_2O constant at 20 and 15 per cent, and to replace progressively SiO_2 by equal weight per cent Al_2O_3. Analyses of the glasses showed that the Na_2O content was less than was planned. In these experiments replacement of SiO_2 by Al_2O_3 was found to increase the density.

The data by Faick, Young, Hubbard, and Finn are included in Table X. 4, and "agree reasonably well with the results reported by Turner and his co-workers if the small amounts of impurities in their glasses are taken into account."

Na_2O-TiO_2-SiO_2. This system was studied by Sheen and Turner.[51] Densities were determined by the pyknometric method, using toluene as the liquid, on grains reduced to 10- to 20-mesh and annealed. Results are given in Table X. 3 and Fig. X. 2. The glasses were of trisilicate composition, with TiO_2 replacing Na_2O. Over most of the range studied, the titania glasses were a little less dense than corresponding lime glasses.

Na_2O-ZrO_2-SiO_2. Dimbleby, English, Firth, Hodkin, and Turner[52] studied three series of glasses in this system. In the first series (748a-h), ZrO_2 replaced Na_2O in a sodium trisilicate glass, giving the series $6SiO_2$, $(2 - x)\ Na_2O, xZrO_2$. In the second series (757a-e), ZrO_2 replaced SiO_2 in the same parent glass, giving glasses of the formula $(6 - x)\ SiO_2 \cdot xZrO_2 \cdot 2Na_2O$. In the third series 797(a-c), Na_2O was held constant at approximately 20 per cent by weight, and ZrO_2 replaced SiO_2. The results are given in Table X. 3. Replacement of Na_2O by ZrO_2 in the trisilicate glasses increased the density. Replacement of SiO_2 in the same glasses increased the density to a slightly greater degree; and in both cases the curve was practically straight.

Na_2O-PbO-SiO_2. This system was studied by Peddle[53] and by Eng-

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[48] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **5**, 277 (1921).

[49] Dimbleby, V., English, S., Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **8**, 173 (1924).

[50] Faick, C. A., Young, J. C., Hubbard, D., and Finn, A. N., *J. Research Natl. Bur. Standards*, **14**, 133 (1935).

[51] Sheen, A. R., and Turner, W. E. S., *J. Soc. Glass Tech.*, **8**, 187 (1924).

[52] Dimbleby, V., English, S., Firth, E. M., Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **11**, 52 (1927).

[53] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 299 and 330 (1920).

lish, Turner, and Winks.[54] Peddle measured two series of glasses of the general formula 100 SiO_2 + 40 (or 20) Na_2O + x moles PbO (series 180 and 181) as well as one (187) in which SiO_2 was held constant at 70, 65, 60, 50, 40, or 30 per cent by weight, and the ratio of Na_2O to PbO altered. The density of the glasses increased with increasing PbO content; and in series 180 and 181, when more than 10 molecules of SiO_2 were present, increasing the Na_2O decreased the density. The soda glasses had a higher density than the corresponding potash glasses. The results are given in Table XVI. 9, and Fig. X. 7.

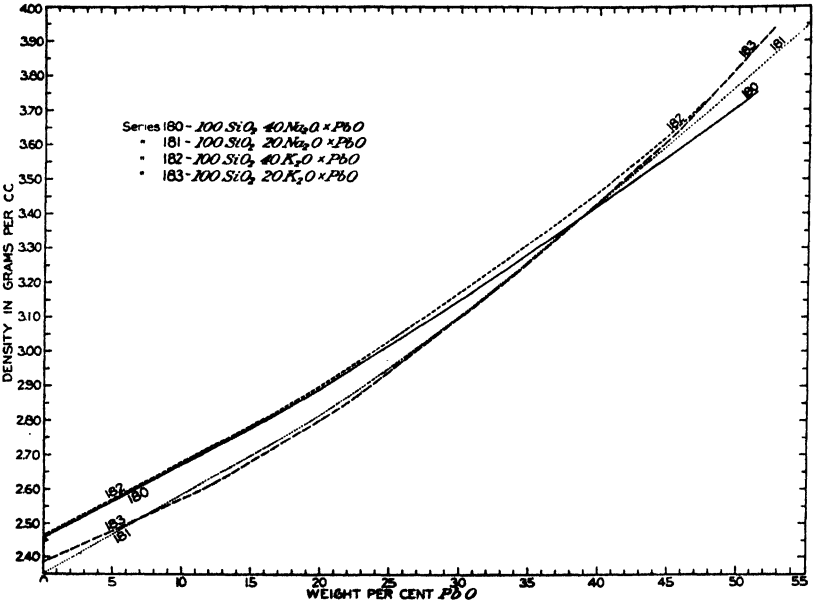

FIGURE X. 7.—Densities of Some Glasses in the Systems Na_2O-PbO-SiO_2 and K_2O-PbO-SiO_2 of the Approximate Compositions Shown. After Peddle.

English, Turner, and Winks replaced Na_2O by PbO in a trisilicate glass, with the results given in Table X. 3. The compositions studied do not overlap enough to enable comparison to be made.

Andersen and Merwin measured the density of some analyzed glasses in this system, with the results given in Table XVI. 7.

Na_2O-Bi_2O_3-SiO_2. Riegel and Sharp[55] made a series of glasses of a composition range chosen to make the glasses comparable with a series of glasses containing lead oxide studied by Peddle (Table XVI. 9, series 180). The results are given in Table XVI. 15. Meltings in the *B*1

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[54] English, S., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **11**, 300 (1927).

[55] Riegel, E. R., and Sharp, D. E., *J. Am. Ceram. Soc.*, **17**, 88 (1934).

series were made in 100-gram lots, in the *B*2 series, in 400-gram lots, and were heated two to three hours at 1300°. Density determinations were made by both the immersion and the pyknometric methods. Bismuth oxide gave glasses denser than those of the same general composition containing lead oxide in place of bismuth oxide.

K_2O-BeO-SiO_2. Lai and Silverman[56] determined the density of some glasses in this system, with the results given in Table X. 6, together with the batch compositions. They used the method of Archimedes with water as the buoyant liquid.

K_2O-CaO-SiO_2. Measurements in this system were made by Peddle[57] (Table XVI. 9) on two series of glasses (167 and 168) of the general composition $100SiO_2 + 40$ (or 20) $K_2O + x$CaO, and hence represent addition of CaO to the glasses $100SiO_2 + 40$ (or 20) K_2O. In addition, measurements were made on glasses (series 175) based on the formula $100SiO_2 + 13.16K_2O + x$CaO, which gave percentages by weight of K_2O equivalent to those of Na_2O in the series $100SiO_2 + 20Na_2O + x$CaO; and on glasses (series 171) in which the SiO_2 was held constant at 70, 65, or 60 per cent while the proportions of K_2O and Na_2O were altered. The glasses were not analyzed. The potash glasses have a lower density than soda glasses having the same percentage-by-weight composition.

Measurements by Merwin and Morey on glasses * covering a much larger range of composition in the ternary system K_2O-CaO-SiO_2 are in Table XVI. 10. Their results confirm and extend Peddle's conclusion that the potash glasses have a smaller density than the corresponding soda glasses.

K_2O-BaO-SiO_2. The results of Peddle[58] on this system are included in Table XVI. 9 and Fig. X. 6. Series 192 and 193 were made of the general formula $100SiO_2 + 40$ (or 20) $K_2O + x$BaO; and in series 201, SiO_2 was held constant at 70, 65, 60, or 50 per cent by weight, and the ratio of BaO to K_2O was altered. The density increased with the content of BaO, and the potash glasses had a lower density than the corresponding soda glasses. The series having the greater K_2O-content (192) had the greater density until 15 molecules of BaO had been added, after which the glasses in series 193 had the greater density.

K_2O-PbO-SiO_2. Peddle[59] measured two series of glasses (182 and 183) based on the formula $100SiO_2 + 40$ (or 20) $K_2O + x$PbO; and a series (187) in which the ratio of K_2O to PbO was altered. The results are given in Table XVI. 9, and Fig. X. 7. The density increased with the PbO content, and the potash glasses had a lower density than the

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[56] Lai, C. F., and Silverman, A., *J. Am. Ceram. Soc.*, 13, 393 (1930).
[57] Peddle, C. J., *J. Soc. Glass Tech.*, 4, 46, 71 (1920).
[58] Peddle, C. J., *J. Soc. Glass Tech.*, 5, 212 and 228 (1921).
[59] Peddle, C. J., *J. Soc. Glass Tech.*, 4, 320 (1920).
* Unpublished results of Merwin, H. E., and Morey, G. W.

corresponding soda glasses. Andersen and Merwin determined the densities of some analyzed glasses in this system, with the results given in Table XVI. 6.

MgO-CaO-SiO_2. Larsen[60] measured the density of a series of glasses on the binary join $CaSiO_3$-$MgSiO_3$ and three other glasses in the system not on the join (Table XVI. 13). Compositions were probably correct to 0.3 per cent. Separate determinations on powder from the same melt usually agreed to ± 0.002, but the difference was somewhat greater when the powders were from different melts. No mention was made of annealing.

Four-Component Glasses

Li_2O-Na_2O-CaO-SiO_2. The densities of these glasses were determined by Waterton and Turner,[61] using the flotation method. The samples, in small pieces, were annealed by heating to the softening point (M_g), cooling to the transformation point (T_g) at a rate of 1° to 2° per minute, then down to room temperature at about 4° per minute. The results are in Table X. 3. The glasses were made to contain constant percentages of SiO_2 (75) and CaO (10), with the proportion of the alkaline oxides changing from glass to glass. Because of the difficulty of separation, the alkalies were determined by difference, after determining SiO_2 and CaO in the conventional manner. As Li_2O replaced Na_2O, the density first rose, then fell, and Waterton and Turner represented it by two straight lines intersecting at the ratio Li_2O to $2Na_2O$.

Li_2O-K_2O-CaO-SiO_2. This system was studied by Waterton and Turner,[61] using the same procedure as with the Li_2O-Na_2O-CaO-SiO_2 glasses, Table X. 3. The density increased with substitution of Li_2O for K_2O. There was no maximum of density, as with the system containing Na_2O, but a break at the composition $Li_2O{:}2K_2O$ was indicated.

Na_2O-K_2O-CaO-SiO_2. Glasses in this system were measured by Peddle[62] with the results given in Table XVI. 9. Series 169 was based on the formula $100SiO_2 + 20K_2O + 20Na_2O + xCaO$; 170 on the formula $100SiO_2 + 10Na_2O + 10K_2O + xCaO$; and in 171 SiO_2 was held constant at 70, 65, or 60 per cent by weight, Na_2O and K_2O were added in equivalent amounts, and CaO was altered. Comparison of these glasses with similarly planned glasses in the ternary systems containing one alkali shows that for two glasses in which the percentages of CaO and SiO_2 are the same, the one having Na_2O alone has a greater density than one having K_2O alone, and when the two alkaline oxides are present in equivalent amounts the density is nearer that of the Na_2O glass than that of the K_2O glass.

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[60] Larsen, E. S., *Am. J. Sci.*, **28**, 263 (1909).

[61] Waterton, S. C., and Turner, W. E. S., *J. Soc. Glass Tech.*, **18**, 268 (1934).

[62] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 59, 71 (1920).

Waterton and Turner[61] measured a series of glasses of the general formula, by weight percentage: $75SiO_2$, $10CaO$, $15(Na_2O + K_2O)$ (Table X. 3) by the same method used by them in studying the glasses Li_2O-Na_2O-CaO-SiO_2. The density increased as Na_2O replaced K_2O. The results were represented by two straight lines intersecting at the equimolecular ratio of the alkaline oxides.

Na_2O-K_2O-BaO-SiO_2. Glasses in this system measured by Peddle[63] are included in Table XVI. 9. In series 194 the compositions were based on the formula $100SiO_2 + 20Na_2O + 20K_2O + x BaO$; in 195, on $100SiO_2 + 10Na_2O + 10K_2O + x BaO$; and in series 202 mixed glasses containing the same percentages by weight of Na_2O and K_2O, with SiO_2 held constant at 70, 65, 60, or 50 per cent, were made by altering the ratio of BaO and alkali. Comparison of these glasses with similarly planned glasses in the ternary system containing only one alkali shows that the dominant effect is the increase in density resulting from the addition of BaO. The Na_2O glasses have a higher density than the K_2O glasses, and the mixed glasses have intermediate density.

Na_2O-K_2O-PbO-SiO_2. Peddle[64] made three series of glasses in this system, and the results are included in Table XVI. 9. Series 184 was based on the formula $100SiO_2 + 20Na_2O + 20K_2O + x PbO$; series 185 on $100SiO_2 + 10Na_2O + 10K_2O + x PbO$; and in series 188 Na_2O and K_2O were each held constant at 10 per cent while the ratio of SiO_2 to PbO was altered. Comparison with the corresponding series containing only one alkali shows that the dominant effect is the increase in density resulting from the increased content of PbO. The Na_2O glasses have a higher density than the K_2O glasses of the same alkali content; and mixed glasses have intermediate density.

Na_2O-MgO-CaO-SiO_2. Five glasses in this system (series 490-92) measured by English and Turner,[65] are included in Table X. 3.

Na_2O-MgO-ZrO_2-SiO_2. Glasses in this system studied by Dimbleby, English, Firth, Hodkin, and Turner[66] are included in Table X. 3. Replacing MgO by ZrO_2 increased the density.

Na_2O-CaO-Al_2O_3-SiO_2. Larsen[67] measured the densities of the glasses on the binary join albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$)-anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) by the pyknometric method, using powder of 100-mesh size. Separate determinations on powder from the same melt usually agreed to ±0.002, but the difference was somewhat greater when the powders were from different melts. The compositions were probably

[63] Peddle, C. J., *J. Soc. Glass Tech.*, **5**, 220 and 228 (1921).

[64] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 320, 330 (1920).

[65] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **6**, 108, 128 (1922).

[66] Dimbleby, V., English, S., Firth, E. M., Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **11**, 52 (1927).

[67] Larsen, E. S., *Am. J. Sci.*, **28**, 263-274 (1909).

correct within 0.3 per cent. No mention was made of annealing. The results are in Table XVI. 13.

Na_2O-FeO-Fe_2O_3-SiO_2. This system was studied by English, Howes, Turner, and Winks.[68] The glasses were made in 28-pound batches, melted at 1400°, and fined at 1350° or 1400°. The batch proportions were of the molecular formula $6SiO_2 \cdot (2 - x) Na_2O \cdot xFe_2O_3$, but about 15 per cent of the Fe_2O_3 was reduced to FeO, as shown by the analyses. The compositions and densities are included in Table X. 3.

K_2O-Rb_2O-CaO-SiO_2. This system was studied by Waterton and Turner,[61] using methods described under the system Li_2O-Na_2O-CaO-SiO_2. The density increased as K_2O was replaced by Rb_2O, and the results, included in Table X. 3, are represented by a straight line.

MgO-CaO-Al_2O_3-SiO_2. Ferguson and Buddington[69] measured the densities of some glasses in the binary system akermanite ($2CaO \cdot MgO \cdot 2SiO_2$)-gehlinite ($2CaO \cdot Al_2O_3 \cdot SiO_2$), using the pyknometric method, with the results given in Table X. 10. The density of crystalline akermanite was 2.944 at 25°, less than that of the glass.

TABLE X. 10.—Densities of Some Glasses in the Binary System Akermanite-Gehlinite.

(After Ferguson and Buddington)

Gehlinite Wt. pct.	Density
100	2.884
75	2.903
50	2.919
25	2.938
0	2.955

Five-Component Glasses

Na_2O-K_2O-CaO-B_2O_3-SiO_2. A series of glasses of the general formula, in percentage by weight: $(75.8 - x)$ SiO_2, $x\,B_2O_3$, 8.56 CaO, 6.86 Na_2O, 7.9 K_2O, was studied by Turner and Winks,[70] with the results given in Table X. 3, Nos. 755-755 p. The density of the glass, powdered to 20- to 30-mesh, was measured by the pyknometric method, using toluene as the liquid. The density increased to a broad flat maximum at 10 to 14 per cent B_2O_3 and then decreased.

Na_2O-K_2O-CaO-Al_2O_3-SiO_2. Berger[71] made an orienting study in this system, and presented his results in a series of groups of plane diagrams in which two of the components were held constant, a scheme of representation devised by Zschimmer; it is not feasible to summarize the results.

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[68] English, S., Howes, H. W., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **12**, 31 (1928).

[69] Ferguson, J. B., and Buddington, A. F., *Am. J. Sci.*, **50**, 131-140 (1920).

[70] Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **9**, 389 (1925).

[71] Berger, E., *Glastech. Ber.*, **5**, 569-79 (1928).

Multicomponent and Commercial Glasses

The densities of many pieces of commercial glass have been measured incidentally to other studies, usually without knowledge of the composition, and such measurements are not reproduced. Many standard types of glass, such as Pyrex resistant laboratory ware and Jena 59^{III}, are of such widespread use that their density becomes a matter of general interest. Fortunately such glasses usually are constant enough in composition for the density commonly given to be used for all but the most exacting work. The densities of many commercial and experimental glasses are given in Table I. 2, and the compositions in Table III. 4. In addition the densities of a number of optical glasses are in Tables XVI. 22, 23, and 26.

Density of Glass at High Temperatures

Most of the measurements of density have been at ordinary temperatures, and the change of density with temperature up to the softening point can be calculated from the numerous measurements of the coefficient of expansion. Some measurements have been made at higher temperatures, but more extensive and accurate determinations are needed.

TABLE X. 11—Densities of Some Glasses at High Temperatures *

After Li

No.	Density at 1206°	Density at 1454°	No.	Density at 1206°	Density at 1454°
2	2.19	2.15	8	2.26	2.20
3	2.42	2.41	9	2.26	2.28
4	2.28	2.35	10	2.31	2.23
5	2.61	2.59	12	2.28	2.23
6	2.46	2.41	13	2.31	2.28
7	2.31	2.26	15	2.48	2.45
			16	2.40	2.43

* Compositions are given in Table VII. 9.

An apparatus for the determination of density at temperatures above the melting point of tin was described by Day, Sosman, and Hostetter.[72] It was an adaptation of Archimedes method with molten tin as the buoyant liquid, and the sample was submerged in a graphite bell. The weights were carried by a graphite yoke, and the position of the bell was determined by an electrical contact. The apparatus was well adapted to the purpose for which it was intended, the measurement of density of minerals; but complications enter into its use with glasses much above the softening point.

Li [73] measured the density at 1206° and 1454° of the glasses used

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[72] Day, A. L., Sosman, R. B., and Hostetter, J. C., *Am. J. Sci.*, 37, 1 (1914).

[73] Li, S. H., Thesis, Univ. of Ill., 1922. Cited by Washburn, Shelton, and Libman, *Univ. Ill. Eng. Expt. Sta. Bull.*, 140 (1924).

by Washburn, Shelton, and Libman in their studies of viscosity and surface tension, with the results given in Table X. 11.

Hänlein [74] used the displacement method, with molten salts as the buoyant liquids. Some experiments were made with molten NaCl, some with the eutectic mixture of NaCl-KCl, and some with the eutectic mixture of LiCl-NaCl. The glass was in a platinum crucible, suspended in the salt bath, and the whole apparatus was evacuated before using to remove gas bubbles. There either was no reaction between salt and glass, or not enough to introduce error greater than the error of measurement. The apparatus was calibrated with optically-clear silica glass. The two glasses used had the percentage compositions: SiO_2, 71.0; Na_2O, 16.5; K_2O, 1.0; MgO, 3.5; CaO, 5.5; Al_2O_3, 0.5; BaO, 2.0 (lime-magnesia glass); and SiO_2, 69.9; B_2O_3, 16.3; Na_2O-K_2O, 5.1; CaO, 0.2; PbO, 6.1 (hard glass). The measurements with the eutectic mixture of LiCl-NaCl gave results differing from those with NaCl-KCl by 0.5 per cent at 1100°, but agreed at 800°. The expansion curve was calculated from the density curve. The results are shown in Fig. X. 8. The transformation point, indicated by the vertical line, was determined from the break in the curve of electrical conductivity versus temperature, using a heating rate of 5° per minute. The measurements of expansion below the transformation point were made on well-annealed samples with a differential expansion apparatus, and the values of density were calculated. They are not to be compared with the density measurements above that point,

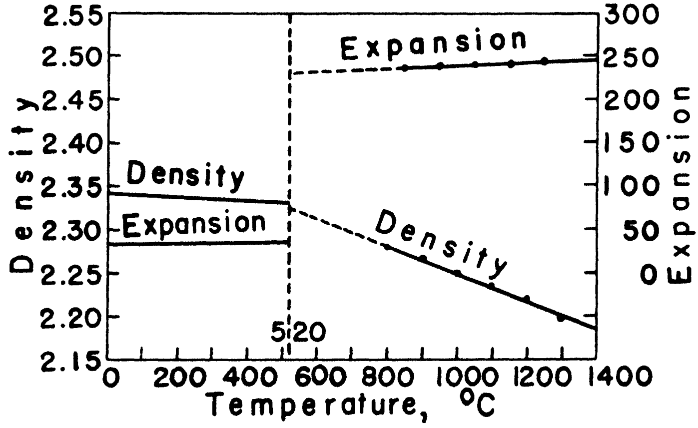

FIGURE X. 8.—Curves showing the Change with Temperature of the Density and the Coefficient of Expansion of a Glass. The Curves above and below the "Transition Point" were obtained by different methods, and no weight should be given to the abrupt changes shown at that point. After Hänlein.

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[74] Hänlein, W., *Glastech. Ber.*, **10**, 126 (1932).

and no weight should be given to the abrupt change in density shown by the curves at the transition point.

Heidtkamp and Endell[75] used Hänlein's method with sodium silicate melts containing more than 65 per cent SiO_2, and they found no appreciable reaction between the NaCl and the sodium silicate melts. The melts containing less than 65 per cent SiO_2 were too fluid for the method, and with them the displacement method was used, with a platinum weight and the melt as the buoyant liquid. The maximum error for the glasses containing more than 65 per cent SiO_2 was estimated as 1.3 per cent; for those containing less SiO_2, 1.2 per cent. The results are in Table X. 12. The compositions given are by analysis. For any one glass, the variation in density with temperature was linear; the lines were divergent at higher temperatures, and intersected at about 1000° to 1120°. When the interpolated values of density at 1000°, 1200°, and 1400° were plotted against composition, the curves rose to a flat maximum showing first a slight increase in density with addition of Na_2O, then a decrease, indicating that Na_2O retained its effect in producing a high coefficient of expansion. There was no correlation with the liquidus curve.

TABLE X. 12—The Density of Sodium Silicate Glasses at High Temperatures

After Heidtkamp and Endell

Per cent SiO_2	Density at Temperature Shown							
79.9	987°	1090°	1146°	1168°	1249°	1265°	1304°	1388°
	2.270	2.255	2.250	2.250	2.240	2.235	2.230	2.220
69.9	1004°	1045°	1150°	1244°	1252°	1342°	1400°	
	2.270	2.265	2.250	2.235	2.230	2.215	2.205	
54.4	1044°	1131°	1170°	1243°	1284°	1340°	1413°	
	2.260	2.245	2.240	2.225	2.210	2.205	2.190	
49.8	1075°	1123°	1259°	1310°	1348°	1421°		
	2.250	2.245	2.215	2.205	2.200	2.180		
44.6	1105°	1122°	1208°	1258°	1305°	1356°	1412°	1428°
	2.245	2.240	2.215	2.205	2.190	2.175	2.165	2.160
39.1	1052°	1144°	1218°	1243°	1319°	1413°		
	2.250	2.220	2.195	2.190	2.165	2.145		

Parmelee and Lyon[76] measured the density of a glass, of the composition given on p. 204, by finding the loss in weight of a 0.55 cc. platinum ball immersed in the molten glass. The results are in Fig. VII. 1.

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[75] Heidtkamp, G., and Endell, K., *Glastech. Ber.*, **14**, 89 (1936).

[76] Parmelee, C. W., and Lyon, K. C., *J. Soc. Glass Tech.*, **21**, 44 (1937).

Chapter XI

The Coefficient of Expansion of Glass

The rate of expansion of glass with temperature is a property of scientific and technologic importance. The change in volume of glass vessels with temperature, and the change in dimensions of thermometer tubing have been the basis for highly accurate measurements of the coefficient of expansion. The successful joining of glass, either to other types of glass, as in the construction of scientific apparatus, in the manufacture of bifocal lenses and radio bulbs, and in the production of flashed glassware,[1] or to other materials such as metals[2] and ceramic bodies, requires that the materials to be joined have nearly the same coefficient of expansion. All these applications necessitate a knowledge of the effect of the change in composition on the rate of expansion of glass; and the coefficient of expansion is a property of glass which is greatly affected by change in composition.

Definitions

The expansivity may be expressed in several ways, of which the commonest is the mean linear coefficient of expansion, α. It is the increase in length $\Delta l = l_2 - l_1$ of the specimen, divided by the original length l_1, when heated over the temperature interval $\Delta t = t_2 - t_1$; that is, the change in length per unit of length per degree rise in temperature,

$$\frac{1}{l_1}\frac{\Delta l}{\Delta t}.$$

Sometimes, instead of the ratio of the differences in length and temperature, $\frac{\Delta l}{\Delta t}$, the slope of the length-temperature curve at the given temperature, $\frac{dl}{dt}$, is used. In that case, if the measurement is referred to the length of the specimen at the given temperature, the value is known as the true linear coefficient of expansion; and if the length at some other temperature is used, the value obtained is that of the true coefficient of expansion referred to the given temperature.

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[1] Sharp, D. E., *J. Am. Ceram. Soc.*, **4**, 219 (1921).

[2] The joining of glass to metals is an important operation which is not discussed in this book. References are: Littleton, J. T., *Phys. Rev.*, **22**, 510 (1923); Housekeeper, W. G., *J. Am. Inst. Elec. Eng.*, **42**, 954 (1923); Hull, A. W., and Burger, E. E., *Physics*, **5**, 384 (1934); Littleton, J. T., *J. Am. Ceram. Soc.*, **18**, 239 (1935).

The cubical coefficient of expansion refers either to the change in specific volume, or to the change in unit volume, with change in temperature. The quantity which usually enters into thermodynamic formulas, the true dilatation, is the rate of increase in specific volume with temperature, $\frac{\delta v}{\delta t}$, at the temperature in question. The coefficient of dilatation more frequently refers to unit volume; and when the volume is that at the temperature in question, the quantity is the true coefficient of dilatation; if referred to the volume at some other temperature, the quantity becomes the true coefficient of dilatation referred to the temperature in question. When, instead of the slope of the volume-temperature curve, the quantity is the difference between initial and final volume at the corresponding temperature, the quantity becomes the mean coefficient of dilatation. In any case, the cubical coefficients are three times the linear coefficients. Failure to define the coefficient frequently leads to confusion.

Methods of Measurement

The methods used for measuring the coefficient of expansion of glass are those commonly used for other materials. They fall into two classes, namely, those which measure the expansion in volume, called volumenometric methods, and those which measure the expansion in length. In the first class is the mercury-in-glass volumenometer, a bulb of glass containing mercury. The expansion of the mercury is measured either by volume or by weight, and from the known true cubical coefficient of expansion of mercury, that of the glass is calculated. This type of apparatus was used by English and Turner[3] in their extensive measurements in the temperature range below 100°. Another type of volumenometer, used by Spaght and Parks[4] in their study of boric oxide, makes use of a metal container for the glass and of mercury as the reference liquid.

Changes in length frequently have been measured by direct observation of the elongation, with micrometer microscopes focused on lines ruled near the ends of the specimen. The elongation sometimes is measured by an optical lever, actuated by the expanding glass rod through a suitable mechanism. The Goerz dilatometer used by Wenig and Zschimmer[5] was of this type. The interferometer affords an excellent method of measuring coefficients of expansion, and an apparatus of this type was described by Peters and Cragoe.[6]

A differential method, in which the expansion of a rod of glass is

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[3] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, 3, 238 (1919).

[4] Spaght, M. E., and Parks, G. S., *J. Phys. Chem.*, 38, 103 (1934)

[5] Wenig, R., and Zschimmer, E., *Sprechsaal*, 62, 855 (1929).

[6] Peters, C. G., and Cragoe, C. H., *Bur. Standards Scientific Papers*, 393 (1920).

compared with that of a standard substance, usually silica glass, is used frequently. The apparatus described by Turner and Winks,[7] and used for numerous studies on glass at temperatures to the softening point, was of this type. Cohn [8] described a self-registering apparatus based on the same principle.

Effect of Heat Treatment

Observations have shown that the rate of linear expansion of glass with temperature is almost constant over a considerable temperature interval up to the annealing range of the glass. More accurate measurements, however, require equations of three or more constants to represent them; and when such high accuracy is in question, the thermal history of the glass becomes of importance, as well as the thermal aftereffect. At higher temperatures, the expansion of glass becomes a less simple matter, and its dimensional changes over the entire range up to the temperature at which it becomes a liquid of low viscosity cannot be represented in any simple manner.

Of particular interest is the rapid change in the coefficient of expansion near the annealing temperature, first indicated by the work of Callender,[9] of Callender and Griffiths,[10] of Holborn and Grüneisen,[11] and of So.[12] Holborn and Grüneisen found that a rod of Jena thermometer glass 59^{III}, 5.7 mm. in diameter and 435 to 438 mm. long, when held at 500° for five hours, shortened 0.79 mm. With the temperature held at 500°, half-hourly readings showed successive contractions of 0.084 mm., 0.038 mm., 0.036 mm., and 0.018 mm. So found that the expansion of glass used was nearly linear up to 400°, and that in the next 50° rise in temperature a considerable contraction took place in unannealed glass.

A thorough investigation of the dimensional changes which take place when glass is heated was made by Peters and Cragoe,[6] using the interferometer method. A summary of their results is given in Table XI. 19, and Fig. XI. 1 gives typical expansion curves. The expansion is nearly linear up to a temperature which is dependent upon the compositions of the glass, and above which the expansion first increases, then decreases. In the first run, shown in curve *A-A*, Fig. XI. 1, the furnace was held at constant temperature for 15 minutes before each measurement was made; in the others a constant heating rate of four degrees per minute was maintained throughout and the observations taken when every fifth fringe passed the reference mark. Below 510° the expansion was nearly linear and reproducible for the different determinations. Between

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[7] Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **12**, 57 (1928).

[8] Cohn, W. M., *J. Am. Ceram. Soc.*, **14**, 265 (1931).

[9] Callender, H. L., *Trans. Roy. Soc. (London), A*, **178**, 161 (1887).

[10] Callender, H. L., and Griffiths, E. H., *Trans. Roy. Soc. (London), A*, **182**, 123 (1891).

[11] Holborn, L., and Grüneisen, E., *Ann. Physik*, **6**, 136 (1901).

[12] So, M., *Proc. Tokyo Math. Phys. Soc.*, **9**, 426 (1918).

510° and 530° (the lower critical point or transition point) the rate of expansion increased rapidly. This rapid expansion continued up to 580° or 590°. With further heating the rate decreased, and an apparent contraction caused by settling began at 608°. Below the first point of inflection the dimensional changes produced by heat were reversible, at least insofar as was determined. Above this point a contraction, which probably was caused by settling or sagging under the weight of the interferometer plate, was superimposed upon the expansion caused by the increase in temperature. At the onset of this stage the rate of contraction was small; the sample first expanded, then at constant temperature slowly contracted. At a higher temperature the contraction proceeded more rapidly, until the rates of the two opposing processes became equal, and on further increase in temperature rapid contraction took place. Similar curves have been obtained by later workers who have

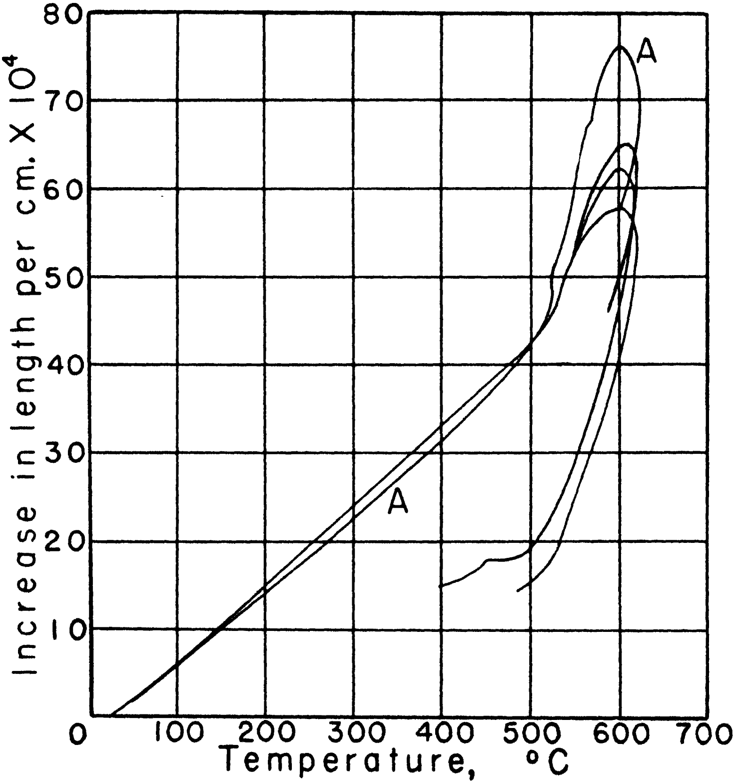

FIGURE XI. 1.—Thermal Expansion Curves of a Barium Flint Glass. After Peters and Cragoe.

carried the measurements to the softening point, including the several studies by Turner and his colleagues, Schönborn,[13] and Pietenpol.[14]

Turner and Winks [15] gave an excellent example of the effect of strain on expansion in the critical region, which is reproduced as Fig. XI. 2.

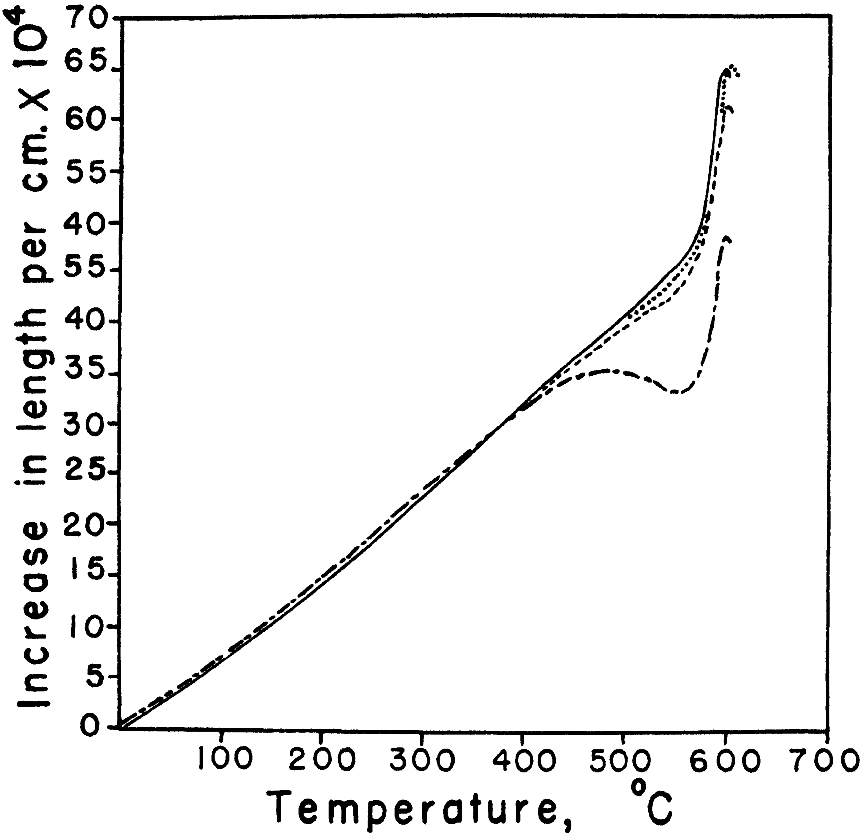

FIGURE XI. 2.—The Effect of Internal Strain on Thermal Expansion. The full curve is that of a well-annealed sample; the lowest curve is that of a quickly-chilled sample, as manufactured; the intermediate curves are those of samples in an intermediate condition of annealing. After Turner and Winks.

The glass had the percentage composition: SiO_2, 56.76; B_2O_3, 19.43; Al_2O_3, 0.90; Fe_2O_3, 0.10; CaO, 8.54; Na_2O, 7.38; and K_2O, 7.14. The continuous curve is that for a well-annealed rod, and immediately below it are two other curves, diverging slightly at about the lower critical tem-

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[13] Schönborn, H., *Keram. Rundschau*, **33**, 17 (1925).

[14] Pietenpol, W. B., *Chem. Met. Eng.*, **23**, 876 (1920).

[15] Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **14**, 84 (1930).

perature, the amount of divergence increasing with the intensity of the strain. The lowest curve represents the expansion of a highly strained rod. On increase in temperature the rod underwent actual contraction up to 557°, and from that point the expansion was rapid. At lower temperatures the curve for the annealed rod is below that of the strained rod, and the two curves cross at about 330°, which indicates that flow took place in the strained rod far below the critical range.

The temperature at which a sudden change in the coefficient of expansion * takes place in a glass heated at approximately four degrees C. per minute has been designated the "transformation point," T_g, considered to be a characteristic temperature for a given composition. When the heating is at the given constant rate, and other conditions are comparable, the transformation point can be located with fair precision.[16]

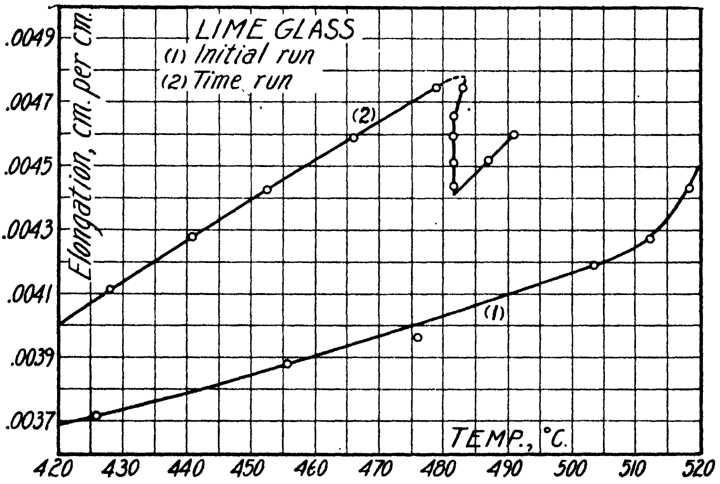

FIGURE XI. 3.—Thermal Expansion Curves of Samples of the Same Glass, having Different Thermal Histories. After Littleton.

There is not unanimity of opinion as to the meaning [17] of the "transition point." Littleton [18] and Morey [19] consider that the effect observed is the result of failure of the glass to reach internal equilibrium at lower temperature with the result that, when the viscosity has been sufficiently diminished by heating, the frozen-in lag is suddenly released. It has

* The transformation point, T_g, has been specified by other means. Cf. p. 461.

[16] Berger, E., Thomas, M., and Turner, W. E. S., *J. Soc. Glass Tech.*, **18**, **79** (1934).

[17] Compare the discussions on pp. 169-172.

[18] Littleton, J. T., *Ind. Eng. Chem.*, **25**, 748 (1933).

[19] Morey, G. W., *J. Am. Ceram. Soc.*, **17**, 315 (1934).

been shown[20] that at temperatures well below the transformation point the properties of the glass change with continued heat treatment, and the time required for the attainment of the equilibrium condition increases rapidly as the temperature is lowered.

The effect of change in heat treatment is illustrated[21] by Figs. XI. 3 and XI. 4. Curve 1 of Fig. XI. 3 gives the normal expansion of an annealed glass heated at 2° C. per minute. The transformation took place at about 510°. The glass was then cooled from 520° sufficiently slowly to be well annealed, but fast enough so that the properties of the 520° state were retained. Curve 2 is the expansion curve then obtained, but at 480° the temperature was held constant for five hours. Fig. XI. 4 shows the constancy of temperature during the five-hour period, and the

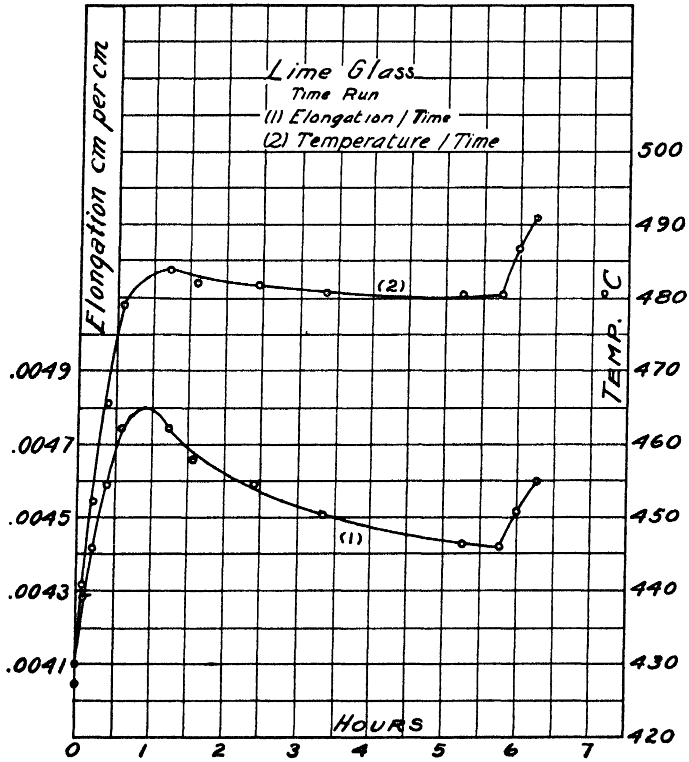

FIGURE XI. 4.—The Change in Length with Time, and Constancy of Temperature, of the Glass of Curve 2, Fig. XI. 3. After Littleton.

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[20] Lillie, H. R., *J. Am. Ceram. Soc.*, **16**, 619 (1933); Morey, G. W., and Warren, B. E., *Ind. Eng. Chem.*, **27**, 966 (1935).

[21] Littleton, J. T., *Ind. Eng. Chem.*, **25**, 748 (1933).

change of length of the specimen. Five hours evidently is almost sufficient for the glass to become stabilized, and it is evident that the expansion change observed by Peters and Cragoe and subsequent workers takes place, not at a fixed temperature, but at a temperature which depends on the thermal history of the glass and the rate of heating of the test specimen. When the heating rate is 4° per minute there is not time for the equilibrium condition to be reached below the transition temperature, and at that temperature the change resulting from the alteration in internal condition of the glass is superimposed on the normal expansion, producing the deviation called the transformation point. That such a point can be observed in the manner described is not doubted, but its theoretical significance has been greatly over-emphasized.

Some recent publications on the coefficient of expansion of glass, especially from the Department of Glass Technology at Sheffield, have held that the expansion curve of a glass at temperatures below the usual annealing range consists of a series of straight lines, intersecting at points called "transition points." The complexity resulting from this interpretation is indicated by the following statement [22] made concerning boric oxide glass: "In very recent work it was found that transition points, some of them of very slight character, occurred at 109°, 125°, 140°, 145°, 155°, and 199°." Littleton,[23] discussing the transition points found by Turner and Winks [24] for a glass consisting of Na_2O and SiO_2, concluded that the experimental results could be represented within experimental error by a cubic equation, and that there was not sufficient justification for regarding the assumed breaks as real.

Turner and Winks [25] made a careful study of the thermal expansion of several glasses up to the annealing temperature, and Seddon and Turner [26] made a study of the effect of slow heating on the observed coefficients of expansion. They are convinced that these change points exist, especially because some glasses, measured in the same apparatus, do not show them, and other glasses do; and consider that the occurrence of transition points at about 120° to 150°, and sometimes at 350°, in glasses of greatly different compositions suggests a common explanation, which has not been found.

Saunders and Tool [27] found that the mean linear expansivity between 20° and 200° C. of Pyrex glass could be changed as much as 10 per cent by subjecting the glass to heat treatments in the range from 450° C. to 750° C. For the original untreated glass, the coefficient of expansion was 3.41×10^{-6}; after treating at about 750°, the coefficient was altered

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[22] Gooding, E. J., and Turner, W. E. S., *J. Soc. Glass Tech.*, **18**, 32 (1934).

[23] Littleton, J. T., *J. Soc. Glass Tech.*, **15**, 262 (1931).

[24] Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **14**, 84 (1930)

[25] Turner, W. E. S, and Winks, F., *J. Soc. Glass Tech.*, **14**, 110 (1930)

[26] Seddon, E., and Turner, W. E. S., *J. Soc. Glass Tech.*, **17**, 324 (1933).

[27] Saunders, J. B., and Tool, A. Q., *Bur. Standards J. Research*, **11**, 799 (1933); RP 626.

to 3.45 × 10^{-6}; treatment at 450° gave 3.07 × 10^{-6}; treatment near 650° restored the original condition. Between 650° and 450° the coefficient decreased with decreasing temperature of heat treatment. A sample of glass having the maximum density, obtained by heating at 450°, on being reheated to 550° increased in volume during the heating by an amount approaching 50 per cent of the cubical expansion during heating from 20° to 550°. A slow rate of heating in the range 450° to 550° thus resulted in an apparent thermal expansion coefficient greatly exceeding the true value in this range. It is general experience that glass quickly cooled has a higher expansivity up to some limiting temperature than when annealed.

Klein[28] heated pieces of borosilicate crown, 5 × 5 × 1 mm., at 2° per minute to a predetermined temperature, then rapidly cooled them in air, and measured the linear coefficient of expansion, with the following results. The first number is the temperature of chilling, the second, $\alpha \times 10^6$: 300°, 6.3; 400°, 6.3; 450°, 6.2; 500°, 5.8; 560°, 6.2; 580°, 6.1; 600°, 6.6; 620°, 6.8; 640°, 7.6; 730°, 8.0; 1000°, 8.0.

Additive Relationship

TABLE XI. 1—Factors for Calculating the Linear Coefficient of Thermal Expansion of Glass*

	Winkelmann and Schott	English and Turner	Gilard and Dubrul
SiO_2	2.67	0.50	0.4
B_2O_3†	0.33	− 6.53	− 4 + 0.1p
Na_2O	33.33	41.6	51 − 0.333p
K_2O	28.33	39.0	42 − 0.333p
MgO	0.33	4.5	0
CaO	16.67	16.3	7.5 + 0.35p
ZnO	6.0	7.0	7.75 − 1.25p
BaO	10.0	14.0	0.1 + 0.14p
PbO	10.0	10.6	11.5 − 0.05p
Al_2O_3	16.67	1.4	2

* Values of $a_1, a_2, \ldots a_n$ in: $\lambda = a_1p_1 + a_2p_2 + \ldots + a_np_n$, in which p_1, etc., are the percentages of the given oxides. $\lambda = \frac{10^8}{l}\frac{\Delta l}{\Delta t}$

† Calculated only for that portion of the curve from 0-12% B_2O_3.

Like many other properties of glass, the coefficient of expansion is roughly an additive property. Over the range in which the expansion is approximately a linear function of temperature, the coefficient of expansion of a complex glass may be calculated on the assumption of additivity by means of the equation

$$\alpha = a_1p_1 + a_2p_2 + \; . \; . \; . \; + a_np_n$$

in which α is the cubical coefficient of expansion, p_1, p_2, . . . p_n are the percentages by weight of the various components, and a_1, a_2, . . . a_n

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[28] Klein, N., *Compt. rend.*, 200, 1320 (1935).

are the constants for the various oxides. The relative effect of the various constituents of glass on expansibility is indicated by these constants. The major constituent of most glasses, SiO_2, is noteworthy in possessing an exceedingly low expansion; two other common constituents, Na_2O and K_2O, both of large atomic volume, increase the thermal expansion greatly; and the remaining constituents usually are of intermediate expansibility.

In Table XI. 1 are assembled the factors for the calculation of the coefficient of expansion proposed by several authors. The work of Winkelmann and Schott[29] is classic. The factors proposed by English and Turner[30] probably are the most reliable, and are self-consistent. They are based largely on trisilicate glasses. Gilard and Dubrul[31] discussed the calculation of the coefficient of expansion from the composition, and proposed a set of factors of the type

$$\alpha \times 10^6 = (ax + bx^2)$$

in which x represents the percentage by weight of a given constituent, and a and b are empirical factors.

An outstanding difficulty in calculating factors for thermal expansion is the value to be assigned to silica. In one method all the factors, including that for SiO_2, are chosen so as to give the best average values over the entire curve. This results in a different factor for SiO_2 for each system, and adjustment is necessary. Another, probably the better method, is to assign to SiO_2 in glass the expansibility it possesses in the pure state, and adjust other factors accordingly.

Since the coefficient of expansion changes with temperatures, it is not to be expected that factors which give approximately correct values for the temperature range from 0° to 100° will be satisfactory at higher temperatures. Turner and Winks[32] gave the following factors for $\alpha \times 10^6$ for Na_2O, deduced from work with binary Na_2O-SiO_2 glasses:

Temperature range	$\alpha \times 10^6$
0°–130°	4.16
130°–250°	4.49
250°–350°	4.76
350°–C_t	4.96

Expansion at Higher Temperatures

The preceding measurements have all dealt with the coefficient of expansion below the annealing temperature. There is a limited amount

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[29] Schott, O., *Vortrag u. Sitzung Ver. Beförd. Gewerbefleisses*, 1892. Winkelmann, A., and Schott, O., *Ann. Physik*, **51**, 735 (1894). Hovestadt, H., "Jena Glass," translation by Everett, J. D. and A., Macmillan, New York, 1902.

[30] English, S., and Turner, W. E. S., *J. Am. Ceram. Soc.*, **10**, 551 (1927), with revisions in *J. Soc. Glass Tech.*, **12**, 760 (1929).

[31] Gilard, P., and Dubrul, L., *Verre silicates ind.*, **5**, 122 (1934).

[32] Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **14**, 110 (1930).

of data on the coefficient of expansion at higher temperatures of either experimental or commercial glasses, which has been discussed in the chapter on density, page 259.

Volarovitch and Leontjewa[33] measured the volume at high temperatures, and from it calculated the coefficient of expansion, by determining by an electrical contact method the expansion of the molten substances in a platinum test tube. K_2SiO_3, $NaBO_2$, and $K_2B_4O_7$ were measured over the temperature ranges 1050°-1200°, 1140°-1250°, and 820°-1250°, respectively. The changes in volume were linear with temperature, and the mean cubic coefficients of expansion, referred to the volume at the lowest temperatures were 2.1×10^{-4}, 3.2×10^{-4}, and 1.8×10^{-4}, respectively. The expansion coefficient of $Na_2B_4O_7$, over the interval 859°-1305°, was 2.6×10^{-4}. The accuracy of the results by this method is questionable.

One-Component Glasses

Boric oxide, B_2O_3. The coefficient of expansion of boric oxide has been studied by several authors, and the results of most of them have been summarized by Gooding and Turner[22] in a table reproduced as Table XI. 2. "It is impossible to state with certainty the precise meaning to be attached to the values given by M. Samsoen, but it appears likely that they represent values taken at the temperature mentioned. Both series of measurements were made with a Chevenard dilatometer, and no reason is apparent for the differences shown unless strained speci-

TABLE XI. 2—Linear Coefficients of Expansion and Critical Temperatures of Fused Boric Oxide.*

Investigator	Temperature							T_g	T_m
	0°	50°	100°	150°	200°	230°	250°		
Samsoen[2] (a)	1430	1475	1518	1565	1612	1641	17,912	245[3]	
(b)			1450		1533		17,890		
	0–100°								
Grenet[3] (a)	1414								
	1446								
			100-200°		264-284°				
Cousen and Turner[4]	1510		1523		1368			239	2
Wenig and Zschimmer[5]	1522		1531						
Seddon and Turner[6]	1541		1438					219	281
					250-286°				
Gooding and Turner[1]	1527		1566		9356			220	285

* Values are of $10^8 \alpha = \frac{1}{l_1} \frac{\Delta l}{\Delta t}$

[1] Gooding, E. J., and Turner, W. E. S., *J. Soc. Glass. Tech.*, **18**, 32 (1934).

[2] Samsoen, M. O., (a) *Bull. Soc. d'Encourag.*, 185, March, 1929, (b) *Compt. rend.*, **181**, 354 (1925); **181**, 517 (1926).

[3] Grenet, L., *Compt. rend.*, 123, 891 (1896); *Bull. Soc. d'Encourag.*, 95, 1557 (1896).

[4] Cousen, A., and Turner, W. E. S., *J. Soc. Glass Tech.*, **12**, 169 (1928).

[5] Wenig, R., and Zschimmer, E., *Sprechsaal*, **62**, 855, 874, 889 (1929).

[6] Seddon, E., and Turner, W. E. S., *J. Soc. Glass. Tech.*, **17**, 324 (1933).

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[33] Volarovitch, M. P., and Leontjewa, A. A., *Z. anorg. allgem. Chem.*, **225**, 327 (1936).

mens were used. The results of L. Grenet were obtained using a modification of Fizeau's interference method."

In the experiments of Seddon and Turner the boric oxide was heated to 1400° for a prolonged period. The measurements were made with a uniform heating rate, in one series, 1° C. per minute; in another series, 10° per hour. The glasses heated at the faster rate were annealed by heating slowly to the softening point (M_g), holding for one hour, then lowering the temperature ½° to 1° per minute for the first 100°, then at 1° per minute to room temperature. For the glasses heated at the slower rate, the approach to the softening point was slower, the period of constant temperature was two hours, and the cooling rate was 10° per hour. The slower rate gave larger values for thermal expansion and the expansion coefficients were a little lower in the range from 100° to 200° than in the range from 0° to 100°. A retrogression connected with the "transition point" began at 200°, and at 211° a very greatly increased expansion set in. This was probably due to change or "stabilization" of the glass.

TABLE XI. 3—True Cubical Coefficient of Expansion of Boric Oxide

After Spaght and Parks

Unannealed		Partially Annealed		Carefully Annealed	
C.°	$3\alpha \times 10^4$	C.°	$3\alpha \times 10^4$	C.°	$3\alpha \times 10^4$
122.1	0.40	120.6	0.56	114.2	0.54
152.3	0.19	152.9	0.59	143.4	0.49
180.4	− 0.19	177.8	0.71	171.8	0.59
204.9	− 1.07	198.3	0.85	199.6	1.18
229.4	0.55	217.1	1.62	226.9	4.35
250.2	4.10	233.1	4.64	250.0	6.13
270.0	6.22	249.1	6.64	270.0	5.92
293.8	6.35				

TABLE XI. 4—Mean Coefficient of Cubical Expansion from 0° C. $\left(3\alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta t}\right)$ and True Coefficients of Dilatation, $\delta v/\delta t$, of Silica Glass

After Sosman

t, ° C.	$3\alpha \times 10^6$	$\delta v/\delta t$	t, ° C.	$3\alpha \times 10^6$	$\delta v/\delta t$
− 250	− 1.05		150	1.55	1.7
− 200	− 0.6	− 2.6	200	1.6	1.7
− 50	− 0.1		300	1.67	1.8
− 100	+ 0.4	− 0.9	400	1.70	1.8
− 50	0.75		500	1.70	1.7
0	1.15	+ 1.1	600	1.68	1.6
+ 50	1.3	1.5	800	1.62	1.5
100	1.45	1.7	1000	1.62	1.9

The results of Wenig and Zschimmer[34] were obtained on material

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[34] Wenig, R., and Zschimmer, E., *Sprechsaal*, **62**, 855, 874, 889 (1929).

which had been melted three hours at 1250°, then 20 minutes at 1500° to 1600°, then cast into rods. They were annealed at 300°, then left in a freely cooling furnace. For the annealed glass the linear coefficient of expansion was found to be: in the range 25° to 75°, 152.2×10^{-7}; in the range 75° to 150°, 153.1×10^{-7}. For a strained glass the coefficient in the lower range was variable; in the range 75° to 150°, it was 167 to 175×10^{-7}.

Spaght and Parks[4] studied the thermal expansion of B_2O_3, using a stainless steel volumenometer, with mercury as the displaced liquid. The material was heated for two hours at 1200°. "Since boron trioxide is a very poor conductor of heat, it was important to allow sufficient time for complete equalization of temperature within the sample.

TABLE XI. 5—Linear Coefficients of Expansion, Transition Points, and Transformation Points in the Ternary System Na_2O-B_2O_3-SiO_2*

After Gooding and Turner

No.	Transition and Transformation Points					Linear Coefficient of Expansion; $\alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta t} \times 10^8$				
	t_1	t_2	t_3	T_g	M_g	$0-t_1$	t_1-t_2	t_2-t_3	t_2-T_g	t_3-T_g
26C	Gradual curvature			230	292	Gradual increase, 1412 to 1474				
26B	Gradual curvature			220	290	Gradual increase, 1386 to 1444				
25B	140	Then gradual curvature		270	329	1102	Gradual increase, to 1330			
6B	130	240 d		320	378	932	10.38		1150	
5B	130	240	300 vd	370	430	849	974	1045		1134
4C	130	240 d	350 vd	430	470	895	1030	1133		1223
34	130	250 d	350 vd	425	472	913	1043	1136		1282
1H	120	240 d	360 d	440	484	1025	1222	1382		1540
14B	100	220	290 d	360	413	1525	1700	1904		2024
22B	100	120 d	330 vd	380	427	1419	1623	1756		1932
27A	130	230	300 vd	140[1]	469	1302	1433	1581		1612
28A[2]	100	200	260 d	470	494	1145	1332	1411		
22C	130	250	350 vd	500	550	999	1134	1210		1290
28C	130	250	350 vd	470	543	1007	1075	1162		1231
28B	130	250	460	520	575	778	912	974		1127
29C	100	220	350	460	530	940	1009	1121		1186
29A	100	240	350 vd	490	530	748	860	913		934
29B	130	250 d		440	480	643	694		709	
30A	130	270	420 d	470	525	734	821	889		958
32C	100	250 vd		360	450	841	930		977	
32	130 vd	240		350	405	827	847		1033	
15D[3]	130	250 d		280	341	929				
15E[4]	130			250	325	1158				
40	130	240	360	395	432	1388	1571	1732		2080
41[5]	100	190 d	250	400	465	1285	1366	1472		
39	130	240	350	475	508	1104	1205	1318		1379
37	100	250	350	525	576	855	982	1062		1131
36	130	250 vd	350 vd	560	598	724	812	837		870
38[6]	130	250 vd	450 vd	560	595	624	680	713		765
42	Gradual curvature			585	610	Gradual increase from 503 to 534				

* Compositions are in Table X. 3.

d = doubtful. vd = very doubtful.

[1] Probably misprint for 440.

[2] $t_4 = 350$; $t_3 - t_4 = 1480$; $t_4 - T_g = 1530$.

[3] $t_1 - T_g = 1111$.

[4] $t_1 - T_g = 1297$.

[5] $t_4 = 350$; $t_3 - t_4 = 1564$; $t_4 - T_g = 1648$.

[6] Gradual curvature likely.

Accordingly, in some cases the temperature of the copper block was maintained constant for periods as long as two and a half hours." Measurements are given in Table XI. 3 for a sample carefully annealed, obtained by cooling from 300° at 5° per hour; in a partially annealed condition, cooled from 300° at 25° per hour; and in the unannealed condition, obtained by cooling the volumenometer and contents in ethyl alcohol. The values given are of the true coefficient of dilatation.

TABLE XI. 6—Linear Coefficients of Expansion of Sodium Silicate Glasses*

After English and Turner

Weight per cent SiO_2	66.91	70.38	74.05	76.27	79.13	81.34	82.83
$10^8\ \alpha$	1346	1240	1138	1035	917	849	755

* $\alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta t}$

Silica, SiO_2. Sosman[35] discussed the coefficient of expansion of silica glass and gave tables showing both the true coefficient of dilatation and the mean coefficient referred to 0°, which are reproduced in Table XI. 4.

Two-Component Glasses

Na_2O-B_2O_3. The glasses from B_2O_3 to $Na_2O \cdot 2B_2O_3$ were studied by Gooding and Turner,[22] using a differential expansion apparatus of Turner and Winks. The compositions of the glasses are given in Table X. 3, the expansion results, in Table XI. 5.

TABLE XI. 7—Linear Coefficients of Expansion of Some Soda-Silica Glasses*

After Samsoen

Weight per cent SiO^2	$\alpha \times 10^6$ at 15°	Transformation temperature (°C)	$\alpha \times 10^6$ after transformation
49.2	12.6	420	83
53.0	15.55	390	72
55.0	18.78	345	65
57	18.52	355	60
60	16.50	420	59
63	13.80	445	50
66.2	13.45	460	42
70	12.85	355	37
76	11.60	350	32
82.5	10.2	420	20
85.3	9.50	445	17
92	7.7	540	11

* $\alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta t}$

Na_2O-SiO_2. English and Turner[36] studied glasses in this system by

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[35] Sosman, R. B., "The Properties of Silica"; Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

[36] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **5**, 121 (1921).

means of a mercury-in-glass volumenometer, with the results given in Table XI. 6. Samsoen[37] used a dilatometric method, with the results given in Table XI. 7. He found a maximum in the coefficient of expansion at 56 per cent SiO_2. The transition temperatures passed through a maximum at the composition of $Na_2O \cdot 2SiO_2$, and through minima at the eutectic compositions. This result has not been confirmed.

Turner and Winks[32] determined the thermal expansion of more glasses over a temperature range extending over the "incipient softening point" (C_t), where the expansion curve took a marked upward trend, to the "upper annealing temperature" (A_t), where the curve bent sharply (Table XI. 8). They used a differential expansion apparatus, described by them in another paper. With glasses containing 88 per cent or more of SiO_2, the point A_t was no longer found on the curves; Navias[38] did not confirm this, but he found a softening point. The point C_t could not be found on the curves for the glasses highest in Na_2O. The several "transition points" could not be found on the curves for the glasses containing the larger amounts of SiO_2, probably because a previous heat treatment had "stabilized" the glasses.

TABLE XI. 8—Linear Coefficients of Expansion, "Incipient Softening Points," C_t, and "Upper Annealing Temperatures," A_t, of Some Sodium Silicate Glasses*

After Turner and Winks

No.	Per cent SiO_2	0-130°	130-250°	250-350°	350-C_t	C_t	C_t-A_t	A_t
114	51.15	1765	1968	2243	(350° − A_t) = 2375			440°
115	55.42	1657	1919	2127	2376	400°	2873	437°
116	60.28	1550	1773	1926	2030	415-20	2320	450°
117	63.48	1419	1653	1769	1960	425	2397	465
118	67.11	1345	1478	1594	1715	450	2003	487
119	70.27	1227	1351	1456	1565	445	2122	495
120	72.80	1146	1253	1357	1426	455	2304	500
121	73.59	1094	1206	1288	1368	455	1852	495
122	74.65	1060	1176	1247	1299	450	1940	508
123	77.30	1015	1086	1124	1209	460	1944	515
					250–C_t			
124	79.93	907	987		1026	455	1627	515
		0-250°						
125	82.34	833			900	470	1144	530
126	85.04	731			756	460	1020	520
			0-A_t					
127	88.17		570					
128	91.60		430					

* Values are of $10^8 \alpha = \frac{1}{l_0} \frac{\Delta l}{\Delta t}$

Seddon and Turner[26] made a study of the effect of slow heating on the expansion of three glasses in this system, using the differential

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[37] Samsoen, M. O., *Compt. rend.*, **183**, 285 (1926).

[38] Navias, L., cited by Hull, A. W., and Berger, E. E., *Physics*, **5**, 384 (1934).

apparatus described by Turner and Winks. The two rates used were 1° and 1/6° per minute. The glasses heated at the rate of 1° per minute were annealed by heating to the softening point (M_g), by holding constant at that temperature for an hour, by cooling at 0.5° to 1° per minute for the first 100°, then at 1° per minute to room temperature. The glasses heated at the slower rate were annealed at M_g for two hours, and cooled at 10° per hour to room temperature (Table XI. 9). The coefficient obtained by the faster heating was usually the smaller. The difference was greater at the lower temperature, and with glass 122 from 300° to 400° the small difference was in the opposite direction. These effects probably were due to the slow approach of the glass to its equilibrium or stabilized condition at low temperatures.

Table XI. 9—Linear Coefficients of Expansion of Sodium Silicate Glasses Heated at Different Rates *

After Seddon and Turner

No.	Weight Per cent SiO_2	0-100° A†	0-100° B	100°-200° A	100°-200° B	200°-300° A	200°-300° B	300°-400° A	300°-400° B
116A	60.71	1541	1560	1438	1494				
122	74.65	1610	1623	1633	1637	1854	1809		
124A	80.77	1113	1144	1161	1171	1229	1232	1285	1288

* Values are of $10^8\ \alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta t}$

† Column A refers to a heating rate of 1° per minute; B to a rate of 1/6° per minute.

B_2O_3-SiO_2. The thermal expansion of glasses in this system was studied by Cousen and Turner,[39] with the results summarized in Table XI. 10. The apparatus was that used by Turner and Winks. The annealing of the glasses was carried out in several cases by heating them in the apparatus as for an expansion determination, and allowing them

Table XI. 10—Linear Coefficients of Expansion * of Boric Oxide-Silica Glasses †

After Cousen and Turner

No.	Lower temperature range 0-100° $\alpha \times 10^8$	Lower temperature range 100-200° $\alpha \times 10^8$	Critical Range Temp. (°C)	Critical Range $\alpha \times 10^8$
816a	1317	1419	270-290	12,000
816b	1181	1260	280-300	10,230
816c	1114	1166	280-300	9,700
816d	870	897	300-320	8,990
816e	719	701	320-340	6,940
816f	576	548	350-370	5,790
816g	498	508	380-400	4,500
816h	475	449	390-410	3,010

* $\alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta t}$

† Compositions are given in Table X. 3.

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[39] Cousen, A., and Turner, W. E. S., *J. Soc. Glass Tech.*, 12, 169 (1928).

to cool slowly; a slow current of dry air was passed through the apparatus when the glasses were rich in B_2O_3. No inflection points were found in the lower temperature range. In all cases the coefficients found were less than would be calculated from an additive relationship.

Three-Component Glasses

Na_2O-BeO-SiO_2. Rencker[40] published some measurements on glasses in this system in the form of curves plotted in triangular diagrams, showing the lines of equal transformation temperature and of equal coefficient of expansion. Table XI. 11 is taken from the abstract, "extracted from the triangular representation of the results." The compositions are given in the abstract as correct to 0.5 per cent. The replacement of either SiO_2 or Na_2O by BeO caused an increase in the transformation temperature, but the coefficients of expansion were scarcely affected by the replacement of SiO_2 by BeO, and were diminished by the substitution of BeO for Na_2O.

TABLE XI. 11—Linear Coefficients of Expansion and Transformation Temperatures of Glasses in the System Na_2O-BeO-SiO_2 from 20° to 400°*

After Rencker

BeO	Na_2O	SiO_2	Transformation Temp. (°C)	$\alpha \times 10^6$
6.5	7.5	86.0	655	5.0
4.0	9.5	86.5	650	5.4
12.5	12.5	75.0	645	7.3
11.0	15.0	74.0	640	8.4
7.5	12.5	80.0	635	7.4
12.0	16.0	72.0	630	8.8
10.0	18.0	72.0	610	9.6
14.0	20.0	66.0	610	10.0
5.0	19.0	76.0	595	10.0
11.0	26.5	62.5	595	12.2
7.5	23.5	69.0	585	11.2
12.0	31.0	57.0	585	13.1
3.5	22.5	74.0	530	10.9
7.0	28.5	64.5	530	12.8
3.0	26.0	71.0	500	11.8
	20.0	70.0	490	10.0
	25.0	75.0	470	11.5
	27.5	72.5	465	12.6
	30.0	70.0	460	13.6
	37.0	63.0		17.0

* $\alpha = \frac{1}{l_0} \frac{\Delta l}{\Delta t}$

Na_2O-MgO-SiO_2. English and Turner[41] studied a series of glasses of the general formula $6SiO_2 \cdot (2 - x)\ Na_2O \cdot xMgO$. The compositions and thermal expansions are given in Table X. 3, Nos. 24 to 28, 329 to 390. The MgO glasses were of lower expansion than the CaO glasses,

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[40] Rencker, E., *Compt. rend.*, **197,** 840 (1933); Abstract, *J. Soc. Glass Tech.*, **18,** 112 (1934).

[41] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **4,** 115 (1920).

both when plotted on a molecular basis and on a weight-per cent basis, as in Fig. XI. 5. A mercury-in-glass volumenometer was used in a temperature range from 25° to 90°. "The glass dilatometers were all annealed before being used."

Na_2O-CaO-SiO_2. Measurements of thermal expansion in this system have been made by several observers. English and Turner[8] made measurements on glasses Nos. 1 to 11, 16 and 17 in Table X. 3; Nos. 1 to 11 were trisilicate glasses in which Na_2O was replaced by CaO. The mercury-in-glass volumenometer used held between 150 and 300 g. of mercury. The temperature range was approximately from 25° to 90°.

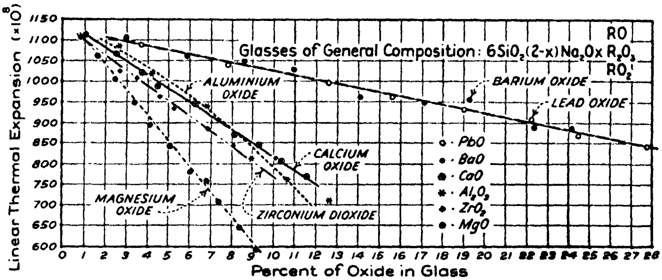

FIGURE XI. 5.—The Effect on the Linear Coefficient of Expansion of Replacing Na_2O by the indicated Percentages of other Oxides in a Glass of the Composition $2Na_2O \cdot 6SiO_2$. After Turner.

Turner and Winks,[7] in a study of the effect of cobalt oxide on the thermal expansion, measured a glass of the composition: SiO_2, 74.52; Al_2O_3, 0.40; Fe_2O_3, 0.04; CaO, 8.14; Na_2O, 16.86, by a differential expansion method. The values of $\alpha \times 10^6$ were:

Temperature range	$\alpha \times 10^6$	Temperature range	$\alpha \times 10^6$
0°–100°	9.02	200°–300°	9.98
0°–200°	9.22	0°–400°	9.78
100°–200°	9.42	300°–400°	10.69
0°–300°	9.47	0°–500°	10.55

They also described the apparatus later used in many studies.

Seddon, Turner, and Winks[42] made measurements on pure glasses, melted in platinum and subsequently analyzed, using the differential apparatus described by Turner and Winks. The first reading (at 25°) was taken with the temperature rising less than 1° per minute, after which the rate of heating was increased to 2° per minute until T_g was reached, when it decreased to 1° per minute. The samples were held at the softening temperature (M_g) for one hour; the temperature was reduced 0.5° to 1° per minute for the first 100°, then 1° per minute down

[42] Seddon, E., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **18**, 5 (1934).

TABLE XI. 12—Linear Coefficients of Expansion of Soda-Lime-Silica Glasses for the Temperature Ranges between "Average Transition Points," Transformation Temperatures, T_g, Softening Temperatures, M_g, and Analytical Compositions*

After Seddon, Turner and Winks

No.	SiO_2	CaO	Na_2O	T_g	M_g	$t_1 = 75°$ 0-75°	$t_2=190°$ 75-190°	$t_3=240°$ 190-240°	$t_4=310°$ 240-310°	$t_5=370°$ 310-370°	370-T_g	T_g-M_g
151	75.94	12.04	12.00	524°	585°	744	760	806	853	881	941	1629
152	75.25	9.37	15.38	500	560	844	878	918	986	1013	1059	1739
153	74.70	6.91	18.39	489	542	916	937	1004	1047	1075	1158	1562
154	74.75	4.80	19.91	457	516	998	1005	1072	1137	1157	1210	1715
155	74.65	2.69	22.66	454	497	1054	1068	1152	1216	1233	1305	1905
156	76.00	12.26	11.74	519	586	723	750	776	846	858	933	1552
157	75.80	10.21	13.99	518	577	796	824	856	913	923	1019	1696
158	81.19	8.07	10.52	515	577	658	654	680	680	740	786	1511
159	74.07	10.01	15.45	512	568	858	887	940	1000	1020	1118	1986
160	70.27	14.08	15.49	520	584	898	938	1006	1057	1087	1199	2117
161	72.87	10.06	16.96	482	542	895	931	1020	1020	1095	1182	1580
162	70.64	14.41	15.00	522	570	874	918	946	957	1028	1141	1672
163	73.21	11.85	14.91	519	562							

* Values are of $10^8 \alpha = \frac{1}{l_i}\frac{\Delta l}{\Delta t}$

to room temperature. The composition, transformation point (T_g), softening temperature (M_g), and linear coefficient of expansion ($\alpha \times 10^8$) for temperature intervals between "average transition points," are given in Table XI. 12. "This term 'average transition point' needs a little explanation. It has already been shown that these transition points vary somewhat in definiteness. Some are strong, others are weak and fugitive. Repetition of a thermal expansion determination on the same sample in some cases brings out transition points not brought to light in the first determination, whilst the reverse may happen, namely, that transition points obtained in the first do not appear in the second determination."

The first five glasses (151-155) were of the general formula $6SiO_2 \cdot (2 - x) Na_2O \cdot xCaO$. It was concluded that the variation in coefficient of expansion of a series of glasses made according to linear variation was itself linear.

Seddon and Turner,[26] in a study of the effect of different rates of heating on expansion, studied two glasses in this system. The first was an experimental melt: SiO_2, 72.35; Na_2O, 15.38; CaO, 9.37; and the second was a window glass: SiO_2, 72.01; Na_2O, 12.70; CaO, 13.11; Al_2O_3, 1.92; Fe_2O_3, 0.20; B_2O_3, 0.17. The annealing procedure was described under the Na_2O-SiO_2 glasses. The linear coefficients of expansion obtained at the two rates of heating, 1° per minute and 1/6° per minute, are shown in Table XI. 13. There was so great a difference between the two glasses that generalizations cannot be made.

TABLE XI. 13—Linear Coefficients of Expansion of Soda-Lime-Silica Glasses, Heated at Different Rates.*

After Seddon and Turner

	0-100°		100°-200°		200°-300°		300°-400°		400°-500°	
	A†	B	A	B	A	B	A	B	A	B
P152	843	839	902	903	950	928	1014	1027	1068	1002
Window	821	851	853	889	922	886	1004	974	1023	995

* Values of $10^8 \alpha = \frac{1}{l_0} \frac{\Delta l}{\Delta t}$

† Column A refers to a heating rate of 1°, B to a heating rate of $\frac{1}{6}$°, per minute.

Schmid, Finn, and Young[43] measured the thermal expansion from 25° to 400° C., to the critical temperature and to the softening temperature, by the interferometer method of Peters and Cragoe, with the results given in Table X. 4. The critical temperature, or the temperature at which the rate of expansion definitely increases, was regarded as the temperature at which a straight line drawn through four or five consecutive points on the expansion-temperature curve departed definitely from a line drawn through the next higher points. The softening temperature

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[43] Schmid, B. C., Finn, A. N., and Young, J. C., *Bur. Standards J. Research*, **12**, 421 (1934).

was regarded as the temperature at which the glass became so soft that its rate of shortening by deformation was equal to its rate of expansion.

Na_2O-ZnO-SiO_2. Glasses in this system of the general formula $6SiO_2 \cdot (2 - x)\ Na_2O \cdot xZnO$, were measured by English, Turner, and Winks[44] by two methods. One of these was the mercury-in-glass volumenometer used in earlier studies by Turner and his colleagues; the other was the apparatus described by Turner and Winks. The results obtained by the first method are shown in Fig. XI. 5 and are given in Table X. 3, together with the compositions of the glasses. The results by the second method, given in Table XI. 14, were obtained up to the upper annealing temperature, and indicated three "quite definite change points" for the three glasses containing up to 4.55 per cent ZnO, and two for the glasses containing from 6 to 11 per cent.

TABLE XI. 14—Linear Coefficients of Expansion of Some Glasses Containing Zinc Oxide *

After English, Turner and Winks

No.	Temperature Ranges (°C)				
788a	0-160	160-250	250-350	350-440(C_t)	440-490(A_t)
	1080	1163	1219	1272	1802
788b	0-160	160-250	250-350	350-435(C_t)	435-490(A_t)
	1057	1119	1192	1252	1842
788c	0-160	160-250	250-370	370-445(C_t)	445-494(A_t)
	1002	1069	1135	1212	1970
788d	0-180	180-250	250-450(C_t)	450-493(A_t)	
	955	1034	1082	1679	
788e/2	0-150	150-300	300-445(C_t)	445-500(A_t)	
	911	1009	1087	1320	
788g/2	0-150	150-250	250-470(C_t)	470-530(A_t)	
	819	871	923	1305	

* Values are of $10^8\ \alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta t}$; Compositions are in Table X. 3.

Fetterolf and Parmelee[45] measured by an interferometer method the expansion of a series of glasses containing about 60 per cent of SiO_2, and with ZnO replacing Na_2O. The results are given in Table XI. 15. They found a factor of 6.17 for ZnO for the calculation of thermal expansion from chemical composition (cf. Table XI. 1).

Na_2O-BaO-SiO_2. Analyzed glasses in this system, of the general formula $6SiO_2$, $(2 - x)\ Na_2O, xBaO$, were measured by English and Turner,[46] with the results given in Table X. 3, series 798a-j. Comparison of the three series of glasses made according to the above formula, and containing CaO, BaO and PbO (Fig. XI. 5), showed that the glasses containing PbO had the smallest thermal expansion, and those containing

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[44] English, S., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **12**, 287 (1928).

[45] Fetterolf, L. D., and Parmelee, C. W., *J. Am. Ceram. Soc.*, **12**, 193 (1929).

[46] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **11**, 425 (1927).

BaO, the largest, when the coefficient of expansion was plotted against moles of oxide to 100 moles of SiO_2.

Fetterolf and Parmelee[45] measured by an interferometer method the expansion of a series of glasses containing about 60 per cent SiO, with BaO replacing SiO_2, with the results given in Table XI. 15. The compositions were calculated from the batch melted. They found a factor of 5.7 for BaO for the calculation of thermal expansion from chemical composition.

TABLE XI. 15—Cubical Coefficients of Expansion of Some Glasses Containing Zinc Oxide or Barium Oxide †

After Fetterolf and Parmelee

No.	SiO_2	Na_2O	BaO	ZnO	R_2O_3	20-100°	100-300°	300-400°
Z6	59.7	32.9		5.8	1.6	435.3	490.5	568.5
Z12	59.9	27.6		11.9	0.6	377.2	436.5	483.6
Z18	59.1	21.6		17.4	1.9	325.5	357.0	402.0
Z24	59.1	16.5		23.8	0.6	262.0	300.0	337.5
Z30	58.8	10.9		29.7	0.5	195.6	208.5	239.2*
B6	60.0	32.3	6.0		1.7	436.5	513.0	572.0
B12	60.1	26.8	12.2		0.9	400.0	468.6	556.8
B18	59.6	20.9	18.2		1.3	371.7	418.5	510.0
B24	59.4	15.7	24.0		0.9	341.1	368.3	415.5
B30	59.4	9.9	30.0		0.7	293.5	324.0	357.0

* From 300-500°.

† Values are of 10^7 (3 α).

Na_2O-B_2O_3-SiO_2. Two series of glasses in this system were studied by English and Turner[47] using a mercury-in-glass volumenometer. One series contained about twenty, the other, about ten per cent Na_2O, with B_2O_3 replacing SiO_2. The compositions and the coefficients of thermal expansion, in the range 25° to 90°, are given in Table X. 3. In the series with twenty per cent Na_2O, replacing SiO_2 by B_2O_3 lowered the coefficient to a broad minimum; in the ten per cent series, to a sharp minimum.

Gooding and Turner[22] studied glasses on the joins $NaBO_2$-SiO_2 and Na_2SiO_3-B_2O_3, the compositions of which are given in Table X. 3, using the differential expansion apparatus of Turner and Winks. The expansion coefficients and the transition points are given in Table XI. 5. It will be seen that a large number of the "transition points" are considered "doubtful" or "very doubtful."

Wenig and Zschimmer[34] measured the coefficient of expansion of glasses in the system Na_2O-B_2O-SiO_2, using a Goerz dilatometer, in the interval from 25° to 150° with the results given in Table XI. 16. Three series of glasses were measured. In Nos. 1 to 7, B_2O_3 was added to a soda-silica glass containing 66.7 per cent SiO_2; in Nos. 8 to 19, Na_2O was held constant at 5, 15, or 25 per cent, and SiO_2 was replaced by

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[47] **English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, 7, 155 (1923).**

B_2O_3; and in Nos. 20 to 26, B_2O_3 was added to the soda-silica glass containing 80 per cent SiO_2. Analyses of the glasses were given. The measurements were made on rods, either drawn or cast, annealed by heating two or three hours at the temperatures given in Table XI. 16, after which the furnace was allowed to cool freely. Examination showed that the glasses were free from strain. The coefficients of expansion were represented by a cylindrical surface in a solid model, in which percentages of Na_2O and B_2O_3 were plotted on the base, and the coefficients perpendicular to the base. This surface could be derived from the empirical formula

TABLE XI. 16—Linear Coefficients of Expansion of Glasses in the Ternary System Na_2O-B_2O_3-SiO_2 *

After Wenig and Zschimmer

No.	SiO_2	B_2O_3	Na_2O	Fe_2O_3 + Al_2O_3	Annealing Temperatures (° C.)	$\alpha \times 10^7$
1	66.84		33.16	0.19	490	141.5
2	63.81	4.33	31.86	0.19	510	133.3
3	61.57	8.28	30.15	0.19	560	125.7
4	59.53	11.33	29.14	0.17	690	118.1
5	53.66	18.05	28.29	0.20	610	115.1
6	55.15	17.60	27.25	0.21	600	110.8
7	55.74	18.29	25.97	0.15	600	105.2
9	80.32	14.63	5.05	0.23	520	33.1
10	75.29	19.99	4.72	0.16	600	33.9
11	71.77	23.78	4.45	0.15	610	37.1
12	74.49	10.76	14.75	0.21	560	71.0
13	71.43	14.24	14.33	0.18	610	69.9
14	65.59	19.94	14.47	0.19	600	70.0
15	61.94	23.92	14.14	0.20	590	69.1
16	65.49	10.12	24.39	0.21	540	105.4
17	61.27	14.57	24.16	0.22	545	100.9
18	55.72	20.17	24.11	0.21	535	100.7
19	51.00	24.86	24.14	0.20	535	100.4
20	79.89		20.11	0.19	500	95.8
21	76.99	4.68	18.33	0.19	500	88.2
22	73.38	8.71	17.91	0.19	550	83.3
23	70.05	12.79	17.16	0.16	550	78.8
24	67.55	16.29	16.16	0.18	575	74.0
25	65.65	19.33	15.02	0.16	570	72.1
26	62.04	22.80	15.16	0.20	550	72.3

* $\alpha = \frac{1}{l_0} \frac{\Delta l}{\Delta t}$

$$\alpha \times 10^7 = 0.0588\,(B_2O_3 - 15)^2 + 3.80\,(Na_2O - 5) + 33$$

in which B_2O_3 and Na_2O represent percentages by weight. Direct comparison with English and Turner, or Gooding and Turner, is not possible because of differences in composition, heat treatment, and temperature range; but there is general agreement within the range 0 to 12 per cent B_2O_3.

Na_2O-Al_2O_3-SiO_2. English and Turner[48] studied a series of trisilicate glasses made according to the formula $6SiO_2 \cdot (2 - x)Na_2O \cdot xAl_2O_3$, with the results given in Table X. 3 (Nos. 441 to 6), which also gives the compositions of the glasses. The effect of alumina is shown in Fig. XI. 5. When the substitution is plotted on a mole per cent basis, the glasses containing alumina show a smaller coefficient of expansion than those containing MgO or CaO; but when plotted on a weight per cent basis, as in Fig. XI. 5, the alumina glasses do not greatly differ from those containing lime.

Dimbleby, English, Hodkin, and Turner[49] studied glasses in which Al_2O_3 replaced SiO_2. In one series (680-3), the plan was to hold Na_2O constant at twenty per cent, in the other series (684, 684*a* and 685), at fifteen per cent, and to alter the percentages of SiO_2 and Al_2O_3 by weight. The results are given in Table X. 3. In these glasses, there was little effect on the coefficient of expansion when SiO_2 was replaced by Al_2O_3.

Na_2O-TiO_2-SiO_2. Sheen and Turner[50] measured the coefficient of expansion from 25° to 90° by a mercury-in-glass volumenometer of a series of glasses of the general formula $6SiO_2 \cdot (2 - x)\ Na_2O \cdot xTiO_2$. The compositions of the glasses and the expansion coefficients are given in Table X. 3. In this series of glasses, TiO_2 was less effective in reducing the coefficient of expansion than MgO, but more effective than CaO.

Na_2O-ZrO_2-SiO_2. The results of measurements on three series of glasses in this system by Dimbleby, English, Firth, Hodkin, and Turner[51] are included in Table X. 3. In the first series (748), having the general formula $6SiO_2 \cdot (2 - x)\ Na_2O \cdot xZrO_2$, replacement of Na_2O by ZrO_2 resulted in a rapid decrease in expansion. For glasses containing approximately equivalent molecular proportions of CaO, MgO, Al_2O_3, and ZrO_2, the corresponding coefficients were: 988, 947, 811, and 808×10^{-8}. In a second series (757), ZrO_2 replaced SiO_2 according to the formula $(6 - x)\ SiO_2 \cdot 2Na_2O \cdot xZrO_2$; and in a third series (797), Na_2O was held approximately constant at 20 per cent, and the percentages of SiO_2 and ZrO_2 were altered from 75 to 65 and from 5 to 15 per cent, respectively. These glasses indicated that ZrO_2 increased the thermal expansion of silicate glasses less than most of the other oxides.

Na_2O-PbO-SiO_2. Mori[52] determined the linear coefficients of expansion of a series of analyzed glasses of the general formula $6SiO_2 \cdot (2 - x)\ Na_2O \cdot xPbO$, with the results given in Table XI. 17.

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[48] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **5**, 183 (1921).

[49] Dimbleby, V., English, S., Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **8**, 173 (1924).

[50] Sheen, A. R., and Turner, W. E. S., *J. Soc. Glass Tech.*, **8**, 187 (1924).

[51] Dimbleby, V., English, S., Firth, E. M., Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **11**, 52 (1927).

[52] Mori, J., *J. Japan. Ceram. Assoc.*, **368**, 176 (1923); *Ceram. Abstracts*, **2**, 244 (1923).

English, Turner, and Winks[53] also studied glasses of the general formula $6SiO_2 \cdot (2 - x)\ Na_2O \cdot xPbO$, with the results given in Table X. 3. The measurements were made with a mercury-in-glass volumenometer. The composition range studied overlapped that studied by Mori, and the agreement between the two sets of results is not close.

Four-Component Glasses

Na_2O-MgO-ZrO_2-SiO_2. Glasses in this system measured by Dimbleby, English, Firth, Hodkin, and Turner[54] are included in Table X. 3. In the series 803 a-e, SiO_2 and Na_2O were held constant at 72 and 20 per cent, respectively, and the ratio of MgO to ZrO_2 was altered. In the series 796 a-e, the same procedure was planned, but by mistake it was not carried out. The effect of replacing MgO by ZrO_2 weight for weight was not large, but there appeared to be some reduction in thermal expansion, despite the much larger molecular weight of ZrO_2.

TABLE XI. 17—Linear Coefficients of Expansion of Soda-Lead Oxide-Silica Glasses*

After Mori

SiO_2	PbO	Na_2O	Al_2O_3	CaO	MgO	$\alpha \times 10^8$
51.21	41.83	5.61	1.23	tr.	0.09	705
52.61	39.24	6.90	1.14	0.10	tr.	729
53.58	37.45	7.88	0.96	0.10	0.03	761
54.10	36.60	8.27	0.97	0.06	tr.	781
54.84	33.96	10.02	1.09	0.08	0.01	844
55.87	31.57	11.35	1.15	0.04	0.02	880
58.52	28.01	12.40	0.98	0.09	tr.	903
60.30	24.33	13.83	1.19	0.33	0.02	934
61.67	22.94	14.06	1.15	0.18	tr.	929
65.95	16.35	16.34	1.15	0.14	tr.	966

* $\alpha = \frac{1}{l_0} \frac{\Delta l}{\Delta t}$

Na_2O-CaO-Al_2O_3-SiO_2. English and Turner[55] studied a series of glasses made by substituting Al_2O_3 for CaO in the parent glass $6SiO_2 \cdot 0.9\ CaO \cdot 1.1\ Na_2O$. The compositions of the glasses and the thermal expansions in the range 25° to 90° are given in Table X. 3, Nos. 458 to 460. The substitution lowered the coefficient of expansion.

Na_2O-FeO-Fe_2O_3-SiO_2. English, Howes, Turner, and Winks[56] studied a series of glasses made according to the formula $6SiO_2 \cdot (2 - x)\ Na_2O \cdot xFe_2O_3$. During the melting, about 15 per cent of the ferric iron was reduced to the ferrous condition, as is shown by the analyses in Table X. 3. The expansions were measured with a mercury-in-glass volu-

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[53] English, S., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **11**, 300 (1927).

[54] Dimbleby, V., English, S., Firth, E. M., Hodkin, F. W., and Turner, W. E. S., *J. Soc. Glass Tech.*, **11**, 52 (1927).

[55] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **5**, 183 (1921).

[56] English, S., Howes, H. W., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **12**, 31 (1928).

menometer from 25° to 90° and also with the differential apparatus described by Turner and Winks, with good agreement over the common temperature range. The results of the former series of measurements together with the composition of the glasses are given in Table X. 3; and those of the latter series together with the transition points are given in Table XI. 18. In general there was diminution of expansion as soda was replaced by iron oxide in these glasses.

TABLE XI. 18—Linear Coefficients of Expansion of Soda-Iron Oxide-Silica Glasses, of Compositions given in Table X. 3 *

After English, Howes, Turner and Winks

No.	$20° - t_1$	t_1	$t_1 - t_2$	t_2	$t_2 - C_t$	C_t	$C_t - A_t$	A_t
814a	1044	130°	1152	250°	1226	435°	2266	492°
814b	998	135	1105	250	1199	450	2757	497
814c	1003	135	1120	250	1214	450	3023	493
814d	859	150	925	250	1137	465	3490	515
814e	847	130	933	250	1016	450	3225	507
814f	839	140	911	240	1019	465	4068	512
814g	769	130	880	240	984	450	3450	500
814h	799	130	900	250	987	450	3242	503
814i	732	130	785	250	857	465	2400	525
814j	673	130	752	240	795	475	2402	531

* Values are of $10^8 \alpha = \frac{1}{l_i}\frac{\Delta l}{\Delta t}$

Na_2O-K_2O-CaO-B_2O_3-SiO_2. The thermal expansions of a series of glasses of the general formula, in percentage by weight: $(75.8 - x)$ SiO_2, xB_2O_3, 8.56 CaO, 6.86 Na_2O, 7.9 K_2O, were measured by Turner and Winks.[57] The compositions of the glasses and the expansion coefficients are given in Table X. 3. Substitution of B_2O_3 for SiO_2 first lowered the coefficient to a poorly defined minimum at about 16 per cent B_2O_3, then increased it slightly.

Multi-Component and Commercial Glasses

The coefficients of expansion of numerous multi-component and commercial glasses are included in Tables I. 2 and XI. 19. Table I. 2, which includes other properties of the same glasses, contains part of the work by Winkelmann, Pulfrich, and other associates of Schott in Jena; other work from the same group is in Table XI. 19. The compositions of these glasses are in Table III. 4. Table XI. 19 also includes the work of Peters and Cragoe,[58] who made the first thorough study of the expansion of glass in and near the annealing range. They used a Fizeau-Pulfrich interferometer. The values given are of the mean coefficient of expansion referred to the original length. The rapid increase in expansion in the upper part of the annealing range is noteworthy.

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[57] Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **9**, 389 (1925).

[58] Peters, C. G., and Cragoe, C. H., *J. Optical Soc. Am.*, **4**, 105 (1920); *Bur. Standards Sci. Papers*, **393** (1920).

TABLE XI. 19—Mean Coefficients of Expansion of Some Miscellaneous Glasses

a. Compositions are in Table III. 3

No.	$\alpha \times 10^6$	Temp. Range (° C.)	Lit. ref.	No.	$\alpha \times 10^6$	Temp. Range (° C.)	Lit. ref.
5	5.6	19–414	1	20	3.6	21–471	1
	40.4	540–562			15.1	552–571	

b. Compositions are in Table III. 4

No.	$\alpha \times 10^6$	Temp. Range (° C.)	Lit. ref.	No.	$\alpha \times 10^6$	Temp. Range (° C.)	Lit. ref.
1	5.27	35 (mean)	2	26	9.0	10– 93	2
	5.52	92 (mean)		29	7.02		4
	5.86	149 (mean)		31	8.23		4
	6.12	212 (mean)		32	5.87		4
5	9.17	18– 97	3	35	6.48		4
6	7.64	39 (mean)	2	36	7.88	11– 99	5
	7.82	55 (mean)		38	8.76		4
	8.26	95 (mean)		40	8.75		4
	8.79	151 (mean)		42	8.33		4
	9.37	217 (mean)		43	8.03	20– 94	5
8	7.79		4	44	8.18		4
11	9.20	37 (mean)	2	47	9.34	18– 99	5
	10.04	93 (mean)		50	5.60	0–100	3
	10.61	151 (mean)		52	5.37	0–100	3
	11.11	212 (mean)		53	3.66	10– 93	5
13	9.03	16– 94	3	70	9.30	18– 93	5
19	5.23	7– 92	3	74	8.71	21–100	5
20	8.14		4				

c. Compositions and descriptions are given in e and f below

No.	$\alpha \times 10^6$	Temp. Range (° C.)	Lit. ref.	No.	$\alpha \times 10^6$	Temp. Range (° C.)	Lit. ref.
1	9.9	19–461	1	9	8.8	22–451	1
	37.3	563–579			34.9	494–512	
2	10.8	20–508	1	10	7.0	23–420	1
	40.1	540–560			29.2	495–511	
3	10.1	23–494	1	11	10.2	22–426	1
	46.0	563–583			55.5	502–522	
4	9.9	21–496	1	12	10.4	24–422	1
	47.7	564–589			54.8	494–507	
5	9.4	21–513	1	13	9.0	22–498	1
	42.4	587–613			39.3	539–562	
6	9.7	23–402	1	14	10.7	23–445	1
	39.6	452–478			30.9	510–534	
7	8.8	22–494	1	15	10.3	22–452	1
	33.1	519–550		16	10.2	22–464	1
8	9.0	23–499	1		31.8	523–552	
	64.9	589–610					

d. Compositions unknown; descriptions given in f below

No.	$\alpha \times 10^6$	Temp. Range (° C.)	Lit. ref.	No.	$\alpha \times 10^6$	Temp. Range (° C.)	Lit. ref.
17	12.0	21–372	1	20	11.6	23–405	1
	23.4	506–525			20.5	509–545	
18	9.1	21–338	1	21	9.0	23–383	1
	23.6	464–483			28.3	456–481	
19	9.8	22–364	1	22	8.3	22–376	1
	28.4	510–551			25.8	460–485	

[1] Peters, C. G., and Cragoe, C. H., *J. Optical Soc. Am.*, **4**, 105 (1920); Sci. Paper, Nat. Bur. Standards, No. 393 (1920).

[2] Reimerdes, in "Jena Glass," Hovestadt, H., translated by J. D. and A. Everett. Macmillan and Co., London, 1902.

[3] Pulfrich, C., in "Jena Glass."

[4] Zschimmer, E., *Silikat Zeitschrift*, **2**, 129 (1914).

[5] Pulfrich, C., *Ann. Physik Chem.*, **45**, 609 (1892).

TABLE XI. 19—(*Continued*)

e. Compositions of glasses in c above

No.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	MgO	BaO	ZnO	PbO	Fe_2O_3	As_2O_3
1*	71.5		13.4	0.1	12.5	0.3				0.1	0.9
2*	72.0		16.2	0.3	10.2					0.1	0.3
3*	72.0		13.7		12.4					0.1	0.1
4*	72.5		13.8	0.2	11.5					0.1	
5*	71.3		10.4	0.4	14.7					0.4	
6	44.3		3.5	5.0	3.0				44.0		0.2
7	58.8	1.7	1.7	8.3			14.3	2.5	12.7		
8	47.6	4.0	2.0	6.0			29.2	9.9			1.4
9	53.9		1.0	7.6	2.0				35.2		0.3
10	54.0		1.0	6.0	2.0				36.7		0.3
11	68.5	3.5	12.0	5.0			9.7	1.0			0.2
12	67.0	3.5	12.0	5.0			10.6	1.5			0.4
13	66.5	7.8	9.8	5.9			7.8	2.0			0.2
14	74.0		17.1		5.8	3.1					
15	74.3		17.2		5.5	3.0					
16	74.0		16.1		7.2	2.7					

* indicates compositions determined by analysis; others were calculated from batches melted.

f. Descriptions of glasses c and d

1, 2, 3,	American-made plate glass	12,	light crown optical glass, BS103
4,	German plate	13,	borosilicate crown optical glass, BS94
5,	French plate	14, 15, 16,	commercial glasses
6,	medium flint optical glass, BS110	17,	"soda" tubing
7,	barium flint optical glass, BS145	18,	"lead" tubing
8,	barium crown optical glass, BS87	19,	"fluorite" tubing
9,	light flint optical glass, BS188	20,	vacuum-tube tubing
10,	light flint optical glass, BS33	21,	fusing-in glass, German
11,	light crown optical glass, BS20	22,	fusing-in glass, Corning Glass Works

Glass No. 6 in Table XI. 19 was Jena borosilicate thermometer glass 59^{III} (No. 56, Table III. 4), which has been measured by several observers. Henning[59] found $\alpha = 4.23 \times 10^{-6}$ from $-191°$ to $+16°$; Holborn and Grüneisen[60] found $\alpha = 6.33 \times 10^{-6}$ from 0° to 500°; and Peters and Cragoe gave 6.38×10^{-6} from 38.5° to 488°.

TABLE XI. 20—Average Coefficients of Expansion, $\alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta T}$, of Pyrex Chemical Resistant Glass

After Buffington and Latimer

Mean Temp.*	307°	273°	233°	202°	158°	121°	99°
Interval	17.9°	49.1°	30.6°	33.2°	54.7°	18.6°	25.1°
$\alpha \times 10^5$	0.37	0.34	0.32	0.29	0.24	0.17	0.11

* Temperatures are in Degrees Absolute.

Glass No. 61 of Table III. 4, which also is in Table I. 2, was Jena "Normal" thermometer glass, which has been much used for low-tem-

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[59] Henning, F., *Ann. Physik*, **22**, 631 (1907).

[60] Holborn, L., and Grüneisen, E., *Ann. Physik*, **6**, 136 (1901).

TABLE XI. 21—Coefficient of Expansion of Some Industrial Glasses *

After Damour and Thuret

Type of Glass	Composition								Misc.	$\alpha \times 10^7$	Range (° C.)	Lower Annealing Temp. (° C.)	Commencement of Fusion (° C.)
	SiO_2	B_2O_3	Na_2O	K_2O	MgO	CaO	Al_2O_3	Fe_2O_3					
Pyrex (A)	80.4	13.0	4.30				1.81	0.49		28	0-400	440	580
Bottle (A)	62.5		8.3	0.4	5.1	18.2	2.7	2.3	SO_3, 0.5	81	0-400	490	580
Bottle (A)	65.30		12.24		1.96	11.40	6.84	1.18	SO_3, 0.78, MnO, 0.22	92	0-400	435	550
Bottle, clear (A) ..	71.60		13.35		2.17	9.40	1.98	0.36	SO_3. 0.88, MnO, 12	92	0-400	395	500
Bottle (S)	77.39		16.18			6.13			Sb_2O_3, 0.19; As_2O_3, 0.11; MnO, 0.10	92	0-400		525
Wine glass (S) ..	72.82		17.78			8.97			Sb_2O_3, 0.18; As_2O_3, 0.14; MnO, 0.11	98	0-400	395	510
Wine glass (S) ..	76.89		15.65	0.75					MnO, 0.10	96	0-400	360	470
Ordinary white (S)	54.32	13.58	19.78	4.70		7.62				119	0-350	370	480
Lithia white (S) ..	55.12	13.78	15.85			7.72			Li_2O, 7.73	114	0-350	350	425
Crystal (S)	51.15	1.88	15.79	1.18					PbO, 29.99	117	0-350	350	435
White enamel (S).	40.16	1.47	12.06	2.00		7.21	2.90		PbO, 25.50; F, 7.10; SO_3, 1.0	111	0-350	350	435
Blue enamel (S)..	39.84	1.46	11.96	1.99		7.15	2.89		PbO, 25.30, F, 7.10; CaO, 0.8	107	0-350	330	435

(A) indicates composition by analysis, (S) by synthesis.

* $\alpha = \frac{1}{l_0} \frac{\Delta l}{\Delta t}$

perature work, especially at Leiden. Several studies from that laboratory have given values for its expansivity, of which the most recent is by Keesom and Bijl.[61] They made measurements at the temperature of boiling liquid hydrogen, oxygen, ethylene and water, and represented their results by the formula:

$$\Delta l = l_o\left\{a\left(\frac{t}{100}\right)+b\left(\frac{t}{100}\right)^2+c\left(\frac{t}{100}\right)^3+d\left(\frac{t}{100}\right)^4\right\}\times 10^{-6}$$

in which $a = 722.0$; $b = 51.6$; $c = 7.49$; and $d = 10.14$. A determination by a mercury-in-glass volumenometer from 0° to 100° gave 242.1×10^{-7} as the mean coefficient of linear expansion referred to 0°.

Buffington and Latimer[62] measured the mean linear coefficient of expansion $\left(\alpha = \frac{l}{l_o}\frac{\Delta l}{\Delta t}\right)$ of Pyrex chemical resistant glass at low temperatures, with the results given in Table XI. 20.

Damour and Thuret[63] measured the coefficient of expansion of some commercial glasses, including some types not studied by others. The compositions of the glasses and the thermal expansions are given in Table XI. 21, which also includes values of the "lower annealing temperature," the temperature at which the coefficient of expansion deviates from a straight line, and values of the "commencement of fusion," the temperature at which expansion ceases.

TABLE XI. 22—Linear Coefficient of Expansion and Softening Points of Some Glasses Containing Beryllium Fluoride

After Heyne

Composition, in Per cent	Softening Point (° C.)	$\alpha \times 10^7$
59 BeF_2, 41 NaF	160	253
58 BeF_2, 30 KF, 12 NaF		237
50 BeF_2, 26 KF, 24 MgF_2	265	216
51 BeF_2, 25 NaF, 24 MgF_2	240	231.5
47 BeF_2, 36 KF, 17 AlF_3	240	241
55 BeF_2, 25 NaF, 20 KF		325

Non-Silicate Glasses

GeO_2. Dennis and Laubengayer[64] gave expansivity curves determined by the National Bureau of Standards, showing that GeO_2-glass was similar in its characteristics to the usual glasses. The average coefficient of expansion from 20° to 420° was about 7.7×10^{-6}, and the softening temperature was about 600°.

[61] Keesom, W. H., and Bijl, A., *Proc. Acad. Sci. Amsterdam,* **32,** 1164 (1929).
[62] Buffington, R. M., and Latimer, W. M., *J. Am. Chem. Soc.,* **48,** 2305 (1926).
[63] Damour, E., and Thuret, G., *Compt. rend.,* **185,** 939 (1927).
[64] Dennis, L. M., and Laubengayer, A. W., *J. Phys. Chem.,* **30,** 1510 (1926).

Beryllium Fluoride Glasses. Heyne[65] prepared a number of glasses containing beryllium fluoride, and measured the softening point and the coefficient of expansion from 20° to 100° on the compositions given in Table XI. 22. The glasses were readily attacked by water and weathered rapidly in moist air, especially if lithium was a constituent.

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[65] Heyne, G., *Angew. Chem.*, **46**, 473 (1933).

Chapter XII

The Elastic Properties of Glass

When a piece of glass is strained by the action of an applied force, on removal of the force the glass returns to its original size and shape, provided the temperature is not too high and the force is neither too great nor applied for too long a time. The property by which the glass regains its original dimensions is called elasticity; a substance is said to be elastic when, on being left free, it recovers wholly or partially from a deformation.[1] Glass is an elastic substance at ordinary temperatures according to this definition, which excludes the long-continued application of a deforming force. A perfectly elastic substance is sometimes defined as one which, when brought to any one state of strain, requires at all times the same stress to hold it in this state, however long it may be kept strained or however rapidly its state may be altered from any other strain, or from no strain, to the strain in question.[2] Glass, in common with most other real substances, is not an ideal solid from the point of view of this definition. The experiments of Berndt [3] (Table XII. 1) illustrated the extent to which glass returns to its original dimensions after deformation. The sample used was a borosilicate crown, near No. 8, Table III. 4, cross-section 2 × 5 mm. The stress is expressed as total load in grams, the strain is in arbitrary units, and the permanent deformation is in millimeters. The values in parentheses represent a repetition of the load of 1011.6 g., under which the piece broke. After the preceding stress of the same amount, however, the test-piece

TABLE XII. 1—The Relation Between Stress and Strain in a Glass

After Berndt

Stress	Strain	Strain/Stress	Permanent deformation
153.5	685	4.46	0.00
253.5	1138	4.49	—0.01
353.5	1593	4.51	—0.01
511.6	2285	4.47	0.00
611.6	2740	4.48	0.00
711.6	3180	4.47	0.00
1011.6	4130	4.48	0.00
(1011.6)	(4580)	(4.53)	0.00

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[1] Tait, P. G., "Properties of Matter," 146, Adam and Charles Black, 4th ed. rev., London, 1899.

[2] Kelvin, Lord, and Tait, P. G., "Treatise on Natural Philosophy," 2, 212, Cambridge Univ. Press, 1895.

[3] Berndt, G., *Z. Instrumentenk.*, 40, 20, 37, 56, 70 (1920).

had returned to its original dimensions; no permanent deformation resulted after loading to the breaking point.

The third column of Table XII. 1 gives the ratio of the strain to the stress producing it; the ratio is constant within the limits of experimental error. That the stress is proportional to the strain is a fundamental property of perfectly elastic substances, and the statement of the proportionality is known as Hooke's Law. Throughout the region in which Hooke's law holds, the material is perfectly elastic by definition, and the limit beyond which the strain is no longer proportional to the deforming stress is called the elastic limit. With many substances the region of higher stress can be investigated, and in such plastic substances the proportionality no longer holds. As illustrated by the experiments of Berndt, glass breaks at its elastic limit, and there is no plasticity at ordinary temperatures.

Griffith[4] found Hooke's law to hold to within the error of measurement, about ±0.3 per cent, and Williams[5] found the stress-strain diagrams to be straight lines.

The constant of proportionality for each type of stress is a characteristic property of a substance. The stress may be applied in various ways, for example, by hydrostatic pressure, producing a pure compression; by torsion, producing a shear; or by bending or tension, each of which produces both compression and shear. The behavior under stress is described by the elastic moduli, each of which represents the ratio of a stress to a strain. The specification of the strains resulting from a system of stresses applied to an elastic substance requires in the most general case the specification of 21 elastic constants, but for the case of an isotropic substance these are reduced to two. The commonly used moduli are the modulus of rigidity, or shear modulus, R; the modulus of compressibility, or bulk modulus, K; and the modulus of extension in tension, or Young's modulus, E. In addition an important elastic constant is Poisson's ratio, σ, the ratio of lateral to longitudinal strain under unidirectional stress. Any two of these four moduli may be regarded as fundamental, and the other two may be calculated from them.

Tait[6] developed the relations among these elastic constants in terms of the deformations resulting from the application of a tension to the two sides of a unit cube. The edges normal to these faces will be elongated by the amount (P), while the other edges will be shorter, each in amount q. When a similar system of stresses is applied to another pair of sides, the result is a shear, and the modulus of rigidity, R, is equal to $P/2(p - q)$, in which P is the force, and p and q are the deformations

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[4] Griffith, A. A., *Trans. Roy. Soc. (London), A*, 221, 163 (1920). See p. 202 for the composition of the glass.

[5] Williams, A. E., *J. Am. Ceram. Soc.*, 6, 980 (1923).

[6] Tait, P. G., "Properties of Matter," 146, Adam and Charles Black, 4th ed. rev., London, 1899.

given above. If a compressive force P be applied uniformly to all sides of the cube, the bulk modulus, K, becomes $P/3(p - 2q)$. The reciprocal of this quantity is the compressibility, β. Young's modulus, E, is P/p; and Poisson's ratio, σ, is p/q. Any one of these moduli can be expressed in terms of any other two. Young's modulus in terms of: (1) the moduli of compression and rigidity, (2) the modulus of compression and Poisson's ratio, and (3) the modulus of rigidity and Poisson's ratio is given by

$$E = \frac{9KR}{3K+R} = 3K(1-2\sigma) = 2R(1+\sigma)$$

Several other systems of expressing the elastic constants have been developed, which have been compared in tabular form by Winkelmann.[7]

Dimensions and Units

Each one of the moduli of elasticity is the ratio of a stress intensity to a percentage strain. The intensity of a stress is the ratio of the number representing total stress to the number representing the area over which the stress is distributed, hence the dimensional formula of a modulus of elasticity is FL^{-2}. When the unit of stress is a weight, as is frequently the case, the conversion factor to change from one system of units to another is ml^{-2}, in which m and l refer to the ratios between the magnitudes of the old and the new units. Thus, to change from pounds per square inch to kilograms per square millimeter, ml^{-2} becomes 0.4559 $(25.4),^{-2}$ or 7.0307×10^{-4}.

When a unit of weight is used as a unit of force, its absolute value changes with the value of gravity; true force units, such as the poundal and the dyne, are independent of gravity, and are to be preferred. The unit used in this book is the bar. A barie is a force of one dyne per square centimeter; the bar is 10^6 baries; the kilobar is 1,000 bars. A bar is not greatly different from a normal atmosphere. The unit in the pound-foot-second system corresponding to the dyne is the poundal. The conversion factor for changing weights used as forces to true force units, and of moduli involving these weights, naturally involves the value of the acceleration of gravity, g; it is taken as 980.665 centimeters per second per second, or 32.1739 feet per second per second. When absolute force units are used, the form of the conversion factor is different from the above. The dimensional formula of a modulus of elasticity, using weight units, is FL^{-2}; the dimensions of force are MLT^{-2}; hence the dimensional formula of a modulus of elasticity, using force units, is $ML^{-1}T^{-2}$. The conversion factor to change from poundals per square foot to baries is, since the same time unit is used in both, ml^{-1}, 14.8816×10^{-9}. Table XII. 2 gives conversion factors for the several units.

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[7] Winkelmann, A., "Handbuch der Physik," 1, 539, Barth, 2nd ed., Leipzig, 1905-9.

Poisson's ratio, the ratio between two quantities of like dimensions, is a pure number, and it is the same whatever system of units is employed.

The elementary treatment of strain assumes that the substance is isotropic, and for crystalline substances such as metals the above interrelations between the elastic constants may be far from the experimental fact. In the case of glasses, the agreement, insofar as a comparison can be made, is fair. For example, from the measurements on Jena 16^{III} (No. 61, Table III. 4) of E, and of σ, the value of compressibility is calculated to be 2.23×10^{-3}, and direct determination gave 2.20 at 0°, 2.26 at 30°.

TABLE XII. 2—Conversion Factors for Pressure and Stress Units

Barye (Dynes per cm.)	mm. Hg. at 0° C.*	Poundal per sq. inch	Pound wt. per sq. inch*	Kg. wt. per sq. cm.*	Bar	Normal * atmosphere	Kg. wt. per sq. mm.*	Kilobar
1.	7.50062×10^{-4}				1.0×10^{-6}	9.86923×10^{-7}		$1. \times 10^{-9}$
1.33322×10^{3}	1.	6.22147×10^{-1}	1.93370×10^{-2}	1.35951×10^{-3}	1.33322×10^{-3}	1.31579×10^{-3}	1.35951×10^{-5}	1.33322×10^{-6}
2.14295×10^{3}	1.60735	1.	3.10808×10^{-2}	2.18520×10^{-3}	2.14295×10^{-3}	2.11493×10^{-3}	2.18520×10^{-5}	2.14295×10^{-6}
6.89471×10^{4}	5.17148×10	3.21739×10	1.	7.03070×10^{-2}	6.89471×10^{-2}	6.80455×10^{-2}	7.03070×10^{-4}	6.89471×10^{-5}
9.80665×10^{5}	7.35557×10^{2}	4.57619×10^{2}	1.42233×10	1.	9.80665×10^{-1}	9.67841×10^{-1}	$1. \times 10^{-2}$	9.80665×10^{-4}
$1. \times 10^{6}$	7.50062×10^{2}	4.66650×10^{2}	1.45038×10	1.01972	1.	9.86923×10^{-1}	1.01972×10^{-2}	$1. \times 10^{-3}$
1.01325×10^{6}	7.6×10^{2}	4.72838×10^{2}	1.46960×10	1.03323	1.01325	1.	1.03323×10^{-2}	1.01325×10^{-3}
9.80665×10^{7}	7.35557×10^{4}	4.57619×10^{4}	1.42233×10^{3}	$1. \times 10^{2}$	9.80665×10	9.67841×10	1.	9.80665×10^{-2}
$1. \times 10^{9}$	7.50062×10^{5}	4.66650×10^{5}	1.45038×10^{4}	1.01972×10^{3}	$1. \times 10^{3}$	9.86923×10^{2}	1.01972×10	1.

* All units containing weights used as forces are at standard temperature, pressure and gravity.

The definition of the elastic properties is of special interest in connection with glass, because it is by means of such definitions that glass is placed by some in the class of solid substances. Indeed, glass has been called the perfect solid because for some types Poisson's ratio is near 0.25, a value assumed to be typical of the perfect solid. Poisson's ratio, however, ranges from 0.13 to 0.32 in the glasses listed in Table I. 2, and the assumption that Poisson's ratio for the "perfect solid" should be 0.25 is not tenable. Bingham[8] said: "Only by the behavior of materials under shearing stresses are we enabled to distinguish between a fluid and a solid. If a body is continuously deformed by a very small shearing

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[8] Bingham, E. C., "Fluidity and Plasticity," 215, McGraw-Hill, New York, 1922.

stress, it is a liquid; whereas if the deformation stops increasing after a time, the substance is a solid. This distinction is theoretically sharp like the distinction between a liquid and a gas at the critical temperature, but just as a liquid may be made to pass into a gas insensibly, so a solid may grade insensibly into a liquid. Glass and pitch are familiar examples of very viscous liquids. Paint, clay slip, and thin mud in a similar manner must be classed as soft solids."

The question as to whether or not a glass is a liquid from the point of view of the elastic properties is a difficult one to answer experimentally. In that connection the question as to whether or not glass will flow under its own weight at ordinary temperatures is an interesting one, which Rayleigh[9] and Spencer[10] attempted to answer. Rayleigh loaded a glass rod 4.9 mm. in diameter, 1 meter between supports, with a load of 300 g. (the rod was broken at the end of the experiments by a load of 1060 g.), and observed an initial depression of 2.8 cm., which persisted without significant alteration for seven years. The final position of the middle point under load was only 1 mm. lower than the initial position; but it was not stated whether or not the rod recovered its original form on removal of the load. Spencer made a similar experiment, using a tube 110 cm. long, 1 cm. diameter, 1 mm. wall, supports 1 m. apart, loaded at the middle with 885 g., which was just short of the average weight necessary to break a number of tubes of the same diameter. After the lapse of six years there was a "permanent" deformation of the middle point of 9 mm. "Both experiments lead to the same conclusion, namely, that glass rods and tubes of mature age do not bend under their own weight," but they do not prove that glass does or does not flow at ordinary temperature. The subsequent discussion of "elastic after-effect" indicates that some flow does take place; and the experiments of Perman and Urry may be corroborative. The experiments of Pulfrich[11] showed that the originally plane ends of a cylinder of borosilicate crown (No. 6, Table III. 4) became concave after having been kept for some time at 96°. Wright[12] stated that even at room temperature prisms and lenses made of strained glass do not retain their shape, and that there is danger of surface warping if the strain exceeds a small limit. There appears to be no doubt that loss of figure resulting from warping does take place in large astronomical mirrors which have not been properly annealed. In this case the sensitivity of the measurement is far greater than in any other test which could be applied, and seems to indicate that there may be flow in glass at ordinary tempera-

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[9] Rayleigh, Lord, *Nature*, 125, 311 (1930).

[10] Spencer, C. D., *Nature*, 125, 707 (1930).

[11] Pulfrich, C., quoted by Hovestadt, H., "Jena Glass," English translation, Macmillan, New York, 1902.

[12] Wright, F. E., "The Manufacture of Optical Glass and of Optical Systems," *U. S. Ordnance Dept., Document No. 2037*, Govt. Printing Office, Washington, 1921.

tures. Whether or not the facts observed are the result of mechanical strain, or of a shift in the "internal equilibrium" in the mass is an open question.

The above results tend to indicate that glass is a truly viscous liquid, that it possesses no true elastic limit, and that it cannot support a permanent load. Griffith,[13] however, stated that glass can support a permanent load at 700°, thus indicating that it is plastic even at comparatively high temperatures. This is not in accord with the usual opinion, and is directly contrary to the result of Washburn, Shelton, and Libman,[14] who stated: ". . . the yield value of the molten glasses is zero, that is, they flow as viscous liquids, not as plastic solids." The problem is one which requires not only more exhaustive experimental work, but also a more rigorous theoretical treatment.

Historical

The earliest determinations of the elastic constants of glass were made by Wertheim and Chevandier,[15] Voigt,[16] and Cornu.[17] Their measurements are of historical interest only, although the method devised by Cornu has been used, with modifications, by several later investigators. Von Kowalski,[18] from bending and torsion experiments, calculated the elastic constants of a glass whose composition was not stated. Indeed, this is a criticism to be applied to much of the data in regard to glass; properties are measured, oftentimes with a high degree of accuracy, but information as to the composition and physical condition of the material is lacking. The classic experiments of Winkelmann and Schott [19] and of Winkelmann [20] are not free from this criticism. They carried out an extensive series of experiments on glasses of a definite type, but the compositions were calculated from batch compositions, and differed from the actual composition by an amount which is not negligible, and which is, furthermore, erratic. Their determinations were criticized by Clarke and Turner [21] on the grounds of a lack of homogeneity and the presence of numerous bubbles. The results of Winkelmann and Schott, however, remain the chief source of information as to the magnitude of Young's modulus for many types of glass. They are supplemented by the work of Straubel,[22] who determined the value of Poisson's ratio for a number of the same glasses. He found the value

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[13] Griffith, A. A., *Trans. Roy. Soc. (London), A*, **221**, 163 (1920).

[14] Washburn, E. W., Shelton, G. R., and Libman, E. E., *Univ. Ill. Eng. Expt. Sta. Bull.*, **140**, 48 (1924).

[15] Wertheim, G., and Chevandier, *Compt. rend.*, **20**, 1637 (1845).

[16] Voigt, W., *Ann. Physik Chem.*, **15**, 497 (1882).

[17] Cornu, A., *Compt. rend.*, **69**, 333 (1869).

[18] von Kowalski, J., *Ann. Physik Chem.*, **36**, 307-22 (1889); *ibid.*, **39**, 155-8 (1890).

[19] Winkelmann, A., and Schott, O., *Ann. Physik Chem.*, **51**, 697 (1894).

[20] Winkelmann, A., *ibid.*, **61**, 105 (1897).

[21] Clarke, J. R., and Turner, W. E. S., *J. Soc. Glass Tech.*, **3**, 260-66 (1919).

[22] Straubel, R., *Ann. Physik Chem.*, **68**, 369-413 (1899).

obtained for σ to be affected by the size of the piece tested, but variation of the distance between knife edges did not consistently affect the results. Andrews, in a discussion of a paper by Perman and Urry[23] criticized Straubel's method in that the separation of the knife edges was not great enough. Jessop[24] found differences of about 1% in both Young's modulus and Poisson's ratio as determined after 1 minute and after 50 minutes, which may indicate viscous flow.

Clarke and Turner studied the effect of systematic change in composition on the properties of a series of glasses. They chose a series simple enough to make possible the correlation of change in proportion of a given component with the change in physical properties. Gehlhoff and Thomas[25] made more extensive experiments but did not analyze their glasses; their results are of more technical than scientific value. Further systematic work of the same kind, in other systems of a limited number of components, is greatly needed. Jessop,[26] Twyman and Perry,[27] Wagstaff,[28] and Searle[29] have written primarily on methods; and they, too, failed to determine the composition of their glasses, though Twyman and Perry gave the batch compositions and the optical constants.

One-Component Glasses

Of the various oxides which enter into the composition of the many types of glass, only two, silica (SiO_2) and boric oxide (B_2O_3), are commonly known in the glassy condition. There is an extensive body of literature in regard to the elastic properties of silica glass which has been discussed at some length by Sosman, whose summarized results are given below. Boric oxide glass, on the other hand, has scarcely been studied.

Silica glass, SiO_2. The data existing in the literature on silica glass have been summarized by Sosman,[30] who gave the following table:

TABLE XII. 3.—Elastic Constants of Silica Glass*

Bulk modulus	K	370 kilobars
Rigidity modulus	R	305 kilobars
Young's modulus	E	700 kilobars
Poisson's ratio	σ	0.14 kilobar

* Unit: 1 kilobar = 10^3 bars = 10^9 dynes per sq. cm.
1 bar = 1.020 Kg./cm.^{2} = 14.50 lb./in.^{2}

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[23] Perman, E. P., and Urry, W. D., *Proc. Phys. Soc. (London)*, 40, 186 (1928).

[24] Jessop, H. T., *Phil. Mag.*, *(6)*, 42, 551 (1921).

[25] Gehlhoff, G., and Thomas, M., *Z. tech. Physik*, 7, 105 (1926).

[26] Jessop, H. T., *Phil. Mag.*, *(6)*, 42, 551-68 (1921).

[27] Twyman, F., and Perry, J. W., *Proc. Phys. Soc. London*, 34, 151 (1922).

[28] Wagstaff, *Proc. Cambridge Phil. Soc.*, 21, 59-65 (1922-3).

[29] Searle, *Proc. Cambridge Phil. Soc.*, 21, 772-80 (1922-3).

[30] Sosman, R. B., "The Properties of Silica," p. 437, Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

Some measurements on the compressibility of silica glass at high temperatures and pressures are given in Tables XII. 8 and 12.

Boric oxide glass, B_2O_3. The only elastic constant of boric oxide glass which has been determined is Poisson's ratio, which Straubel[22] found to be 0.283.

Two-Component Systems

No systematic investigation has been made of the variation of elastic constants with composition in a binary system. The only binary glasses on which data are available are a few studied in the course of other investigations.

Three-Component Systems

The first systematic study of the effect of change in composition on elasticity was that of Clarke and Turner,[31] who determined Young's modulus for a series of glasses of the general formula $(Na_2O + CaO) \cdot 3SiO_2$, in which the Na_2O content ranged from 25 to 13 per cent, the CaO content from 0 to 12 per cent. The compositions of their glasses, as determined by analysis, and the values of Young's modulus are given in Table XII. 4. Glass 16 does not belong in the series and No. 11 is discordant. A second sample of the same melting gave a similar result, but a melt made to have the composition $0.9\,Na_2O \cdot 1.1\,CaO \cdot 6SiO_2$ (SiO_2, 75.2%; Na_2O, 11.9%; CaO, 12.9%), but presumably not analyzed, gave a value of E of 749.4 in harmony with the remainder of the series. There was a regular increase in elasticity with CaO content, and the results were represented by the linear equation $E = 13.9y + 565.6$, in which y = weight per cent CaO.

TABLE XII. 4—Young's Modulus for a Series of Soda-Lime Glasses

After Clarke and Turner

No.	SiO_2	Na_2O	CaO	MgO	Al_2O_3	Fe_2O_3	E (Kilobars)
1	74.05	25.34	0.21	tr.	0.24	0.14	567.2
2	73.92	23.80	1.50	tr.	0.21	0.14	581.5
3	74.08	23.00	2.61	tr.	0.28	0.15	605.6
4	74.07	21.50	3.81	tr.	0.38	0.14	621.0
5	73.78	20.78	4.50	0.15	0.58	0.19	630.2
6	73.18	19.38	6.26	0.21	0.30	0.61	657.0
7	74.41	17.20	7.45	0.24	0.31	0.40	667.2
8	74.99	16.00	8.16	0.26	0.42	0.09	683.0
9	74.96	14.88	9.36	0.28	0.45	0.16	689.8
10	74.59	14.22	10.38	0.30	0.38	0.21	710.9
11	74.93	13.02	11.68	0.31		0.17	(677.8)
16	66.71	12.72	18.17	0.85	1.41	0.31	818.2

Gehlhoff and Thomas[25] determined Young's modulus on a series of

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[31] Clarke, J. R., and Turner, W. E. S., *J. Soc. Glass Tech.*, 3, 260-66 (1919).

glasses derived from a two-component glass containing 18% Na_2O, 82% SiO_2 by weight, by replacing SiO_2 by one of the oxides Na_2O, K_2O, MgO, CaO, ZnO, BaO, PbO, B_2O_3, Al_2O_3, or Fe_2O_3. Two series of Na_2O-K_2O-SiO_2 glasses were made; one in which SiO_2 was replaced by K_2O, the other in which Na_2O was replaced by K_2O. The results were given in a series of diagrams, which is reproduced in Fig. XII. 1. Replacing SiO_2 by either Na_2O or K_2O resulted in a decrease in elasticity, and replacing Na_2O by K_2O resulted in a slightly increased elasticity. All other oxides increased the elasticity, although PbO had but little effect.

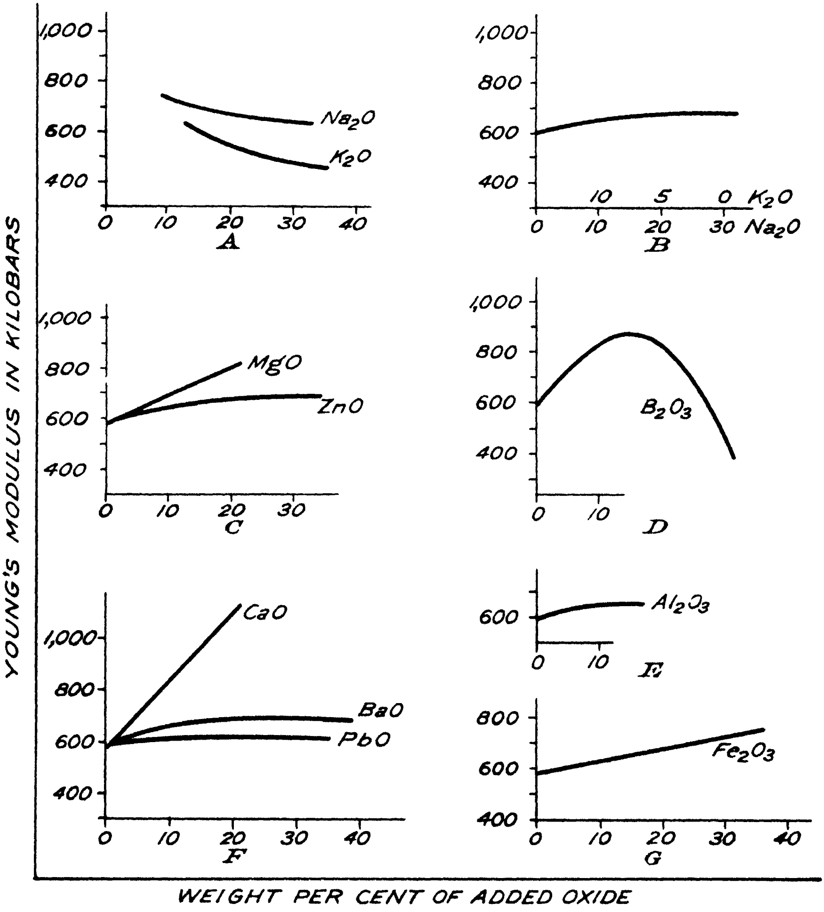

FIGURE XII. 1.—The Effect on Young's Modulus, in a Glass containing 18 per cent Na_2O, and 82 per cent SiO_2, of Replacing SiO_2 by the indicated Percentages by Weight of other Oxides. After Gehlhoff and Thomas.

The curve for B_2O_3 passes through a well-marked maximum, and it is probable that the Al_2O_3 curve would have a similar shape.

Fetterolf and Parmelee[32] determined Young's modulus for some soda-zinc oxide-silica, and some soda-barium oxide-silica glasses. They used a cantilever beam, with the beam 20 cm. long ground to size; the other dimensions were not given. The glasses were not of high quality. Each had about 60 per cent SiO_2, with a ratio of Na_2O to ZnO or BaO altered; the analytical compositions are in Table XI. 15. Duplicate determinations showed a mean deviation from the mean of 8 parts in 1000. Following are average values for Young's modulus in kg. per mm.^{2}: (1) Zinc oxide glasses: Z6, 4950; Z12, 5570; Z18, 5780; Z24, 5910; Z30, 6480; (2) Barium oxide glasses: B6, 5360; B12, 5240; B18, 5590; B24, 5600; B30, 5830.

Horak and Sharp[33] studied the effect of substitution of ZrO for CaO in a series of four glasses, each of which contained 74 per cent SiO_2, 17 per cent Na_2O. The initial glass, *A*, contained 9 per cent CaO and no ZrO_2; *B*, 8 per cent CaO, 1 per cent ZrO_2; *C*, 7 and 2; and *D*, 5 and 4. Values for Young's modulus, when the glasses were measured on a beam supported at two points and loaded in the middle, were: *A*, 439; *B*, 367; *C*, 325; *D*, 275 kilobars. The modulus of rigidity was measured by the torsion pendulum method, using fibers 1 mm. in diameter, 3 ft. long. The values obtained were: *A*, 266; *B*, 251; *C*, 243; *D*, 238 kilobars.

Multi-Component Systems

Most of the data in the literature pertain to commercial glasses, systems of from four to eight or even twelve components. Such determinations are of value only in respect to the piece of glass measured, and in lesser degree, in regard to the particular glass type. The glasses are too complicated, and the data too scanty, to permit the assigning of any particular part of the elasticity to any one component, even if the underlying assumption that the property is colligative had been substantiated. Nevertheless, Winkelmann and Schott,[34] from a series of experiments on such glasses, obtained factors by means of which they proposed the calculation of Young's modulus from the composition. Their first paper contained such a series of factors, but on attempting to apply these factors to the additional glasses contained in the second paper, they found marked discrepancies. Accordingly they divided the glasses into three groups, giving each oxide an independent factor in each group. Many of the experimental results on which the factors were based are in Table I. 2, together with the values of Poisson's ratio, determined by

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[32] Fetterolf, L. D., and Parmelee, C. W., *J. Am. Ceram. Soc.*, **12**, 193 (1929).

[33] Horak, W., and Sharp, D. E., *J. Am. Ceram. Soc.*, **18**, 282 (1935).

[34] Winkelmann, A., and Schott, O., *Ann. Physik Chem.*, **51**, 697 (1894); Winkelmann, A., *ibid.*, **61**, 105 (1897).

Straubel.[22] The serial number refers to Table III. 4, in which are given the compositions of the glasses; additional properties of some of these glasses are given in appropriate places. The compositions were all calculated from the compositions of the batches melted, which differ from the true compositions to an unknown degree. The factors given by Winkelmann and Schott for the calculation of Young's modulus are given in Table XII. 5. Examination of their results shows an agreement within the experimental error between the observed and the calculated values of Young's modulus, but this is not so much a justification of the additive hypothesis as an indication of the crudity of the measurements. Clarke and Turner [21] found discrepancies amounting to 28 per cent when their own experimental results were compared with the values calculated using Winkelmann and Schott's factors; and they calculated a new set of factors, even for adventitious ingredients amounting to a few tenths of a per cent. Their factors also are given in Table XII. 5.

TABLE XII. 5—Factors for Calculating Young's Modulus from Chemical Composition

	Winkelmann and Schott [1]			
	A	B	C	Clarke and Turner
SiO_2	6.9	6.9	6.9	3.9
B_2O_3		5.9	2.5	
Na_2O	6.0	9.8	6.9	10.8
K_2O	3.9	6.9	2.9	
CaO	6.9	6.9		23.5
BaO		6.9	2.9	
ZnO	5.1	9.8		
PbO	4.5		5.4	
MgO		3.9	2.9	29.4
Al_2O_3	17.6	14.7	12.7	11.8
Fe_2O_3				11.8
P_2O_5			6.9	
As_2O_5	3.9	3.9	3.9	

[1] Factors under A are for glasses free from B_2O_3, P_2O_5, BaO, MgO; under B, for glasses free from PbO, P_2O_5; under C, for borosilicates, lead borosilicates, and phosphates.

In addition to these more extensive studies, several investigators have published results on isolated glasses of known composition. Griffith [13] gave Young's modulus for a glass of the composition: SiO_2, 69.2; Na_2O, 0.9; K_2O, 12.0; CaO, 4.5; Al_2O_3, 11.8; MnO, 0.9, as 621 kilobars, Poisson's ratio, 0.251. Twyman and Perry,[27] using a glass whose batch composition was SiO_2, 54.83, Na_2O, 6.23, K_2O, 4.30, PbO, 34.64, and optical properties $n_D = 1.5759$, $\nu = 41.3$ found Young's modulus to be 619.8 and Poisson's ratio, 0.196. Berndt [35] found Young's modulus to be 798.9 for a borosilicate crown, n_D, 1.616, ν, 64.0 (No. 8, Table III. 4). Straubel [22] made an extensive study of Poisson's ratio, using Cornu's method; his glasses were mostly those used by Winkelmann and Schott, and his

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[35] Berndt, G., *Z. Instrumentenk.*, 40, 20 (1920).

TABLE XII. 6—Compressibilities of Some Natural and Artificial Glasses*

After Bridgman

Glass	30°		75°	
	a	b	a	b
Pyrex	3.042×10^{-3}	7.1×10^{-8}	3.068×10^{-3}	4.96×10^{-8}
Corning 714x	2.744	4.90	2.810	5.0
Corning 722Q	2.451	1.33	2.538	− 4.28
Corning, SiO_2-free glass	1.716	− 10.4	1.754	− 10.65
Tachylyte Torvaig	1.910	− 11.22	1.949	− 11.32
Pitchstone Meisses	2.545	− 5.54	2.543	− 5.78
Tachylyte Kilauea	1.353		1.401	− 9.28

* Numbers given are the constants in the equation $\Delta V/V_0 = ap + bp^2$; pressure in kilobars.

the calculation of the effect of pressure on Young's modulus and Poisson's ratio (see p. 314). They were: *A*, a potash lead silicate of very high lead content; *B*, "Pyrex"; *C*, a soda-potash lime silicate; *D*, a soda zinc borosilicate; *E*, a soda lead borosilicate, opacified with calcium and aluminum fluorides; and *F*, a soda lime silicate containing a small percentage of boric oxide. Bridgman used a method in which the bulk compressibility was calculated from the linear compressibility, and he found the values given in Table XII. 7.

The increase of compressibility with the increase in pressure found by Bridgman for Pyrex chemical resistant glass was confirmed by Adams and Gibson,[43] who measured directly the bulk compressibility. They gave as the most probable value of the cubic compressibility: $10^5 \beta = 304.5 + 1.42 P$ in reciprocal kilobars at 25° C. They also confirmed the observation of Bridgman that silica glass exhibits the greatest increase of compressibility with pressure of any substance yet examined, and gave for the most probable value of the cubic compressibility of silica glass: $10^5 \beta = 268.9 + 15 P$.

TABLE XII. 7—Compressibility of Some Glasses*

After Bridgman

Glass	30°		75°	
	a $\times 10^7$	b $\times 10^{12}$	a $\times 10^7$	b $\times 10^{12}$
A	30.54	− 24.3	30.60	− 22.6
B	30.12	+ 6.1	29.72	+ 6.7
C	24.69	− 22.0	25.44	− 21.2
D	25.97	+ 4.0	26.30	+ 0.2
E	27.78	+ 2.5	27.71	+ 3.8
F	23.29	− 6.1	23.92	− 10.1

* Values of $\Delta V/V_0 = -(ap + bp^2)$; pressure in kg/cm².

Glasses *A*, *C*, *D*, and *E*, and "ordinary Pyrex laboratory glass" (No. 20, Table III. 3), and silica glass were measured by Birch and Dow[44]

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[43] Adams, L. H., and Gibson, R. E., *J. Wash. Acad. Sci.*, **21**, 381 (1931).

[44] Birch, F., and Dow, R. B., *Bull. Geol. Soc. Am.*, **47**, 1235 (1936).

at a series of temperatures, the highest of which was, in each case, between 300° and 400°. The results are in Table XII. 8; and in Fig. XII. 2 values of the average compressibility,

$$\chi_t = -\frac{1}{V_0}\left(\frac{\delta V}{\delta P}\right)_t,$$

to 10,000 kg./cm. are plotted against temperature. "The results for the glasses support the conclusion that the appearance of a negative coefficient of compressibility is possible only below a certain temperature, which depends on the composition of the glass. Thus, for glasses *A, D,* and *E,* this temperature is about 220°, for "Pyrex," 270°; for pure silica glass it lies above 400° and was not reached in these experiments. The other glass, *C,* exhibited a positive and nearly constant temperature coefficient from the beginning. It should be noted that an increase in compressibility with temperature means thermal expansion decreasing with pressure, and conversely, a negative temperature coefficient of compressibility requires a positive pressure coefficient of thermal expansion.

TABLE XII. 8—Compressibility of Some Glasses at High Temperatures and Pressures * up to 10,000 Atmospheres †

After Birch and Dow

t	$a \times 10^4$	$b \times 10^6$	$\chi^1 \times 10^4$
	Silica glass		
11	24.94	− 33.3	28.27
100	25.18	− 26.7	27.85
247	24.09	− 17.3	25.52
390	24.09	− 6.5	24.74
	Pyrex glass		
5	30.40	− 0.8	30.48
100	29.54	− 1.0	29.64
217	27.35	− 6.7	28.02
385			28.58
	Glass A		
12	30.96	20.4	28.92
100	31.45	29.7	28.48
218	29.54	18.5	27.69
231	30.45	22.9	28.16
316	32.69	20.1	30.68
322	32.73	23.1	30.42

t	$a \times 10^4$	$b \times 10^6$	$\chi^1 \times 10^4$
	Glass C		
8	23.61	17.7	21.84
100	24.52	16.7	22.85
15	23.66	13.9	22.27
100	24.51	13.1	23.20
230	26.60	17.0	24.90
313	27.61	15.7	26.04
	Glass D		
9	24.91	− 17.7	26.68
100	25.78	− 9.2	26.70
220	25.23	− 4.2	25.65
227	25.45	− 1.2	25.57
318	25.90	− 1.9	26.09
318	25.20	− 5.4	25.74
319	27.16	+ 11.0	26.06
	Glass E		
7	27.85	− 1.6	28.01
100	27.54	− 1.7	27.71
218			27.21
316	28.53	− 5.4	29.07

* Pressure Unit = 10^3 kg/cm² = 0.9806 kilobar.

† Values of a and b in the equation: $-\Delta V/V_0 = ap - bp^2$; and of $\chi^1 = -\frac{1}{V_0}\left(\frac{\delta V}{\delta P}\right) = a - 10{,}000b$.

"The shapes of the curves in Fig. [XII. 2], the high values of the compressibility, and the rapid changes with temperature fit well with the conception of an essentially liquid nature for the vitreous state. This same sort of irresponsible variation of compressibility with temperature has been demonstrated by Bridgman for a number of true liquids at high pressure and in the temperature range from 0° to 35°. There is another feature of the compressibility of glasses which has,

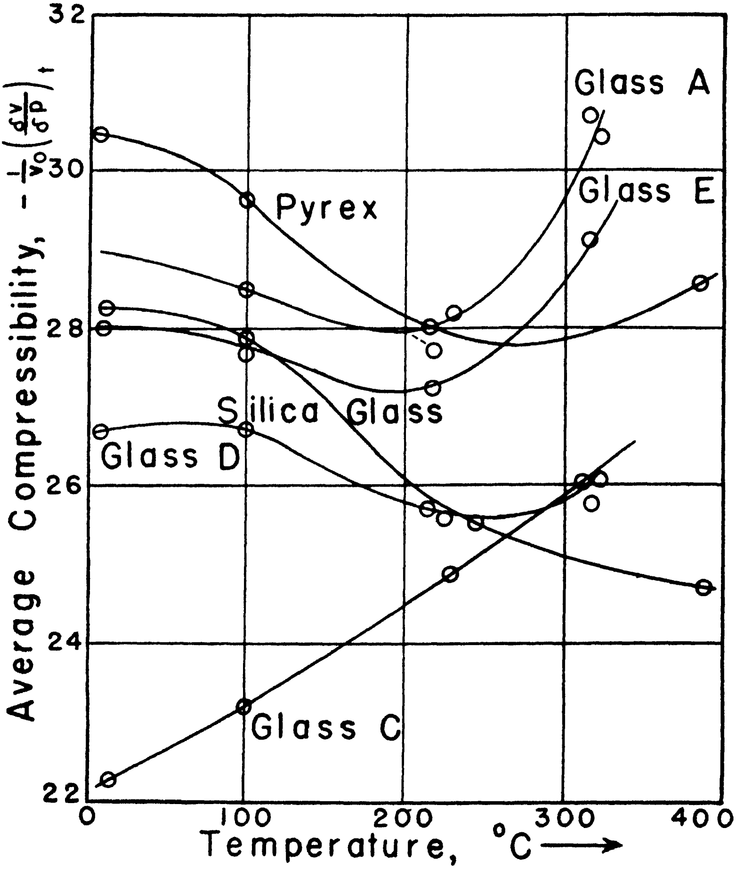

FIGURE XII. 2.—Average Compressibilities of Some Glasses at High Temperatures and Pressures. Compare Table XII. 8. After Birch.

however, no counterpart in the behavior of ordinary liquids; this is the increase of compressibility with pressure already observed by Bridgman for glasses *D* and *E*, for "Pyrex," and for silica glass. There seems to be a tendency for this abnormality also to disappear at higher temperatures, although the experimental uncertainty as to the exact value of the curvature is too great to permit a more definite statement. In one case, glass *D*, after a number of exposures to a temperature of over 300°, the curvature finally became normal; that is, the compressibility decreased with pressure."

Effect of Temperature on Elastic Constants

The difficult problem of determining the effect of temperature on elasticity has been attacked by few investigators. Von Kowalski [45] found that the elasticity coefficient diminished with increasing temperature, but did not state the kind of glass used. Winkelmann [46] made the only extended contribution to the subject; his results serve more to emphasize the difficulty of the investigation than to provide reliable data. He found that at higher temperatures the deflection for a given load increased rapidly as the load was left on; and therefore it was necessary to take readings immediately after loading. The elasticity was greatly affected by the previous thermal history of the sample. For example, when a piece of

TABLE XII. 9—Effect of Temperature on Young's Modulus*

After Winkelmann

No. Table III. 4	Glass Type	$E_{20°}$	$\log_{10} \alpha$	$\log_{10} \beta$	$t_{\text{max.}}$
1	496/644	752	$\bar{9}.018$	0.428	482
3	506/602	655	$\bar{4}.618$	0	448
4	511/640	740	$\bar{4}.352$	0	475
7	513/573	684	$\bar{5}.912$	0.065	409
10	517/609	709	$\bar{4}.369$	0	433
11	517/602	654	$\bar{4}.575$	0	394
19	545/503	549	$\overline{15}.452$	0.706	383
25	571/430	609	$\overline{10}.973$	0.499	374
27	573/575	744	$\bar{6}.923$	0.165	427
40	645/341	540	$\overline{24}.492$	0.945	340
43	751/276	539	$\bar{8}.634$	0.401	357
48	507/614	492	$\bar{4}.449$	0	281
55		738	$\bar{5}.543$	0.082	460
57		721	$\bar{5}.114$	0	482
58			$\bar{4}.616$	0	434
59		652	$\overline{15}.401$	0.717	433
60		741	$\overline{11}.092$	0.553	407
61		730	$\bar{6}.435$	0.232	426
64		604	$\bar{5}.696$	0.113	455
66		577	$\bar{4}.193$	0	417
68		532	$\overline{13}.897$	0.643	413
69		798	$\bar{5}.330$	0.094	486
72	558/670	631	$\bar{6}.230$	0.255	412

* $E_t = E_{20} [1 - (t - 20)]$; range, room temperature to $t_{\text{max.}}$. Unit 10^3 bars.

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[45] von Kowalski, J., *Ann. Physik Chem.*, **39**, 155 (1890).

[46] Winkelmann, A., *Ann. Physik Chem.*, **61**, 105 (1897).

glass was heated, the elasticity as measured immediately after cooling was found to have been increased, but then it slowly decreased with time. After several repeated heatings with intervening cooling, the elasticity became constant. The constant values so obtained are those given in Table XII. 9; they are considerably higher than those given for the same glasses in Table I. 2, doubtless because of the heat treatment. Winkelmann found that some glasses gave a linear relation between elasticity and temperature, but with the majority the elasticity fell off more rapidly. The relation between temperature and Young's modulus was represented by the relation

$$E_t = E_{20}\,[1 - \alpha\,(t - 20)\beta],$$

in which E_t and E_{20} are Young's modulus at $t°$ and at 20°, and α and β are empirical coefficients. His results are assembled in Table XII. 9; the first column gives the reference number of the glass, from which its approximate composition can be obtained from Table III. 4; the second and third columns, values of log α and log β, respectively, and the last column gives the highest temperature to which the glass was heated.

The experimental results led to no satisfactory conclusion as to the effect of composition on the temperature coefficient of Young's modulus. Winkelmann suggested that probably the simultaneous presence of Na_2O and K_2O favors the decrease in elasticity with temperature, the effect being partially nullified by the presence of B_2O_3. It also appears probable that the presence of lead causes the elasticity to fall off more rapidly, but the effect is not proportional to the amount of lead present.

Winkelmann pointed out that there are two methods of expressing his experimental results: the first ignores the change in dimensions of the test-piece as the result of thermal expansion, and the second applies a correction for this expansion. The results quoted above are uncorrected for thermal expansion; the requisite data for applying the correction were not available for the majority of glasses, and in the two cases in which the correction was made the data were not satisfactory. Applying this correction to glasses III. 4. 57 and III. 4. 1, which were noteworthy as showing the smallest falling off of Young's modulus with temperature, indicates that the true elasticity was independent of temperature.

Wandersleb [47] later repeated unpublished work of Winkelmann, which showed that in some glasses containing large amounts of Sb_2O_3 the elasticity increased with increasing temperature. The compositions were not given, but it was stated that four glasses, all borosilicates, containing 3.5, 3.5, 20, and 21 per cent Sb_2O_3 showed an increase in Young's modulus with temperature, while two other glasses, containing 10 and 15 per cent Sb_2O_3, gave the usual decrease. The abnormal glasses gave temperature-elasticity curves with maxima at about 200°, Young's modulus being

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[47] Wandersleb, E., *Ann. Physik,* *(4)*, **8**, 367 (1902).

about two per cent greater at the maximum than at 15°. The above correction for thermal expansion was not made.

The experiments of Birch and Dow, included in the discussion of compressibility, were made at temperatures up to from 300° to 390°, and are probably of greater accuracy than any of the above measurements.

Badger and Silverman[48] measured Young's modulus at temperatures up to 446° by measuring the extension under load. The extension measured was that produced by increasing the load from 400 grams to 500 grams, and from the result a value of the modulus, called a "chord modulus of elasticity," was calculated. The average diameter of the fiber was 0.43 mm., the length, 143.2 mm.; and the average stress at loads of 400 and 500 grams was 3.652 and 4.336 bars, respectively. The composition of the glass was: SiO_2, 68.10; $Na_2O + K_2O$, 18.59; MgO, 4.09; CaO, 5.84; and $Al_2O_3 + Fe_2O_3$, 3.38. The fiber was annealed by heating to 550° and allowing it to cool slowly in position in the furnace. The results are given in Table XII. 10; the unit of E is the kilobar.

TABLE XII. 10—Change of Young's Modulus with Temperature

After Badger and Silverman

E (kilobars)	658	645	641	633	629	595	578	567	560
Average Temp (° C)	25	100	150	200	250	300	350	400	450

The modulus decreased slowly to about 250°, at a rate given by the equation $E_{25^\circ}^{250^\circ} = 659.3 - 0.125t$, then decreased rapidly. From 350° to 450° the change is given by: $E_{350^\circ}^{450^\circ} = 639.0 - 0.18t$. The duration of the loading was not given.

Stong[49] measured Young's modulus on a "Corning bulb glass," composition not given, strain point 480°, annealing point 510°. At the beginning of the first run (Curve 1, Fig. XII. 3), the sample showed about 200 mμ per cm. birefringence. This run was made on a heating schedule of three hours per 50° C. temperature interval. The furnace was allowed to come to constant temperature, and measurements were made about two hours after each temperature increase, except that the furnace was at 450° for five hours before measurements were made. After the measurement at 450° the furnace was cooled at the rate of 50° C. for each three-hour interval, and measurements were made at the several temperatures during cooling. After its removal from the furnace, the sample was almost completely free from strain, and the dimensions had increased by about 0.1 per cent. To investigate the effect of heat treatment, the sample was held at the annealing temperature for 15 minutes, was cooled 200° at one-half degree per minute, and a second run

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[48] Badger, A. E., and Silverman, W. B., *J. Am. Ceram. Soc.*, **18**, 276 (1935).

[49] Stong, G. E., *J. Am. Ceram. Soc.*, **20**, 16 (1937). *Cf.* p. 316.

(Curve 2) was made under the same conditions as the first run. The modulus of elasticity showed a regular decrease with increasing temperature, and the rate of decrease increased rapidly as the temperature approachd 450° C. Samples having different thermal histories gave different modulus-temperature curves.

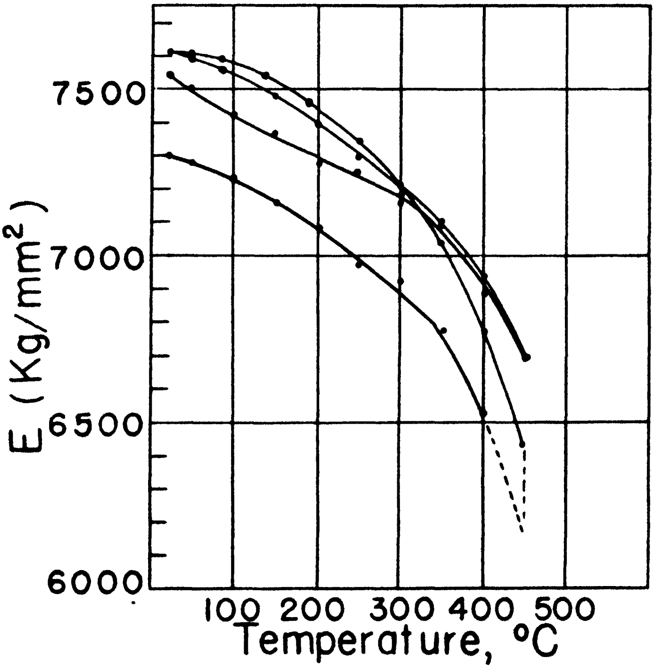

FIGURE XII. 3.—The Change in Young's Modulus with Temperature, with a Heating Rate of 50° C. in Three Hours. After Stong.

Taylor, McNamara, and Sherman,[50] using annealed fibers of a soda-lime-silica glass, found that the deformation immediately below the "transformation point" could be analyzed into an instantaneous (within 5 seconds) elastic distortion, a delayed elastic distortion, and a truly viscous flow. The elastic effects were reversible on removal of the load.

TABLE XII. 11—Young's Modulus for a Glass Fiber at Various Temperatures
After Taylor, McNamara, and Sherman

Temp. (° C)	475	500	525
E_1 (Kg/mm²)	4.4	3.5	2.4
E_2 (Kg/mm²)	2.3	2.4	2.4

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[50] Taylor, N. W., McNamara, E. P., and Sherman, J., *J. Soc. Glass Tech.*, **21**, 61 (1937).

Values of Young's modulus for the instantaneous elongation (E_1) and for the total elastic elongation after 100 minutes (E_2) are given in Table XII. 11; the "transformation point," determined from thermal expansion measurements, was 515° C. The value of E_1 decreased with rising temperature, and E_2 appeared to be independent of temperature in the range studied. The delayed elastic distortion required less than five seconds above 520° C., which was interpreted to mean that glass behaves as an ordinary liquid above this temperature.

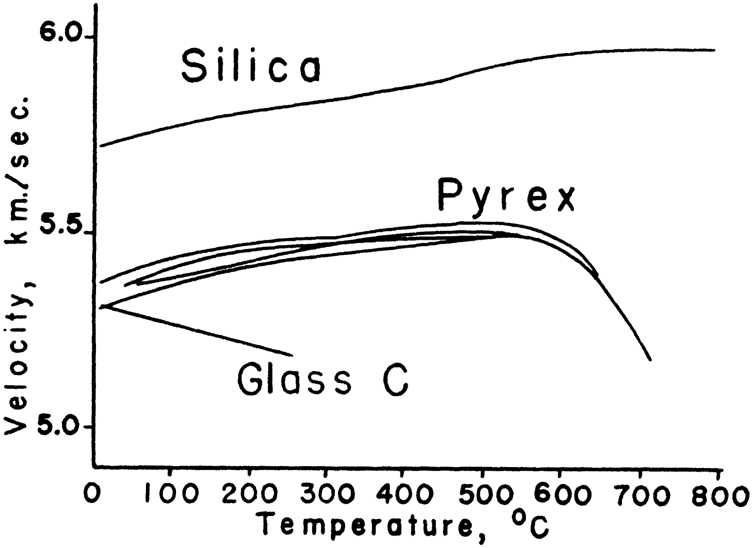

FIGURE XII. 4.—The Velocity of Sound in Glass. After Ide.

The preceding measurements have all been made by static methods, in which the rate and the manner of loading become increasingly important factors as the temperature is raised. A dynamic method of determining Young's modulus is afforded by measuring the velocity of sound in glass, which is connected with Young's modulus by the relation:

$$\text{velocity} = \sqrt{E/d},$$

in which d is the density. Ide[51] measured the velocity of sound in (1) an obsidian, (2) silica glass, (3) Pyrex chemical resistant glass, and (4) a soda-lime glass, glass *"C"* studied by Bridgman (p. 306) and by Birch and Dow (p. 307), by means of an oscillatory system, which produced vibrations with a period of 0.00007 second. The results

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[51] Ide, J. M., *J. Geol.*, **45**, 689 (1937).

obtained for the velocity of sound in the several types of artificial glass at several temperatures are shown in Fig. XII. 4; the velocity decreased with temperature in glass *C*, increased in silica glass, and first increased, then decreased in Pyrex chemical resistant glass. In the Pyrex, the decrement of the vibrations showed no noticeable variation until about 650° C.; then it increased rapidly until the observing system became practically non-oscillatory above 700° C. On cooling the glass to room temperature, the velocity of sound returned to a value of 1.3 per cent higher than at the beginning of the measurements; and on repeating the experiments, the irreversible effects shown in the figure were given. It would be of interest to apply this method to the study of the rate of "stabilization" of glass in the upper part of the annealing range. The values of *E* at various temperatures calculated by Ide are given in Table XII. 12.

TABLE XII. 12—Values of Young's Modulus, in Kilobars, at Several Temperatures, Calculated from the Velocity of Sound

After Ide

Temp. (° C.)	Obsidian	Silica	"Pyrex"	Glass C
0	694.0	722.	630.0	703.
100	696.3	736.	647.5	697.
200	697.3	747.	657.7	683.
300	698.9	754.	667.5	657.
400		763.	673.0	
500		775.		
600		783.		
700		786.		
800		787.		

Effect of Pressure on Elastic Constants

Bridgman[52] studied the effect of pressure on the rigidity of five types of glass, the compositions of which are given in the discussion of compressibility. A differential method was used, and "the accuracy was not sufficient to justify an attempt to determine departures from linearity." The final results obtained with different varieties of glass are shown in Table XII. 13. The units are kg./cm^2. The table also includes values for Young's modulus and Poisson's ratio, calculated from the given values of rigidity and the values for compressibility previously given. "The negative sign of the effect was a surprise to me; by very crude analogy with the effect of pressure in enormously increasing the viscosity of liquids, I had expected a rather large increase of shearing modulus. On reflection, however, the negative sign does not seem so strange in view of the fact that the compressibility of a number of different kinds of glass has been shown to increase with increasing pressure.

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[52] Bridgman, P. W., *Proc. Am. Acad. Arts Sci.*, **63**, 401 (1929).

In fact, turning to the table of compressibilities, it will be seen that just those glasses, *B*, *D*, and *E*, which have the abnormal increase of compressibility with pressure also have the largest decrease of shearing modulus, and the two glasses, *A* and *C*, which are most normal in their decrease in compressibility also have the smallest numerical change of shearing modulus under pressure."

Effect of Strain on Elastic Constants

When glass is allowed to cool without special precautions from the temperature at which it can be worked or shaped, it is in a strained condition, the outermost layers being under compression, the innermost under tension. The complete removal of this strain is a matter of considerable difficulty, and is rarely accomplished except in the case of optical glass required for special instruments. Strain is usually present in glass, and its effect on the elastic properties thus becomes of importance.

Table XII. 13—Effect of Pressure on Elastic Moduli of Some Glasses*

After Bridgman

Glass	R	$\frac{1}{R}\left(\frac{\delta R}{\delta P}\right)_t$ $\times 10^3$	E	$\frac{1}{E}\frac{dE}{dP}$ $\times 10^3$	σ	$\frac{1}{\sigma}\frac{d\sigma}{dp}$ $\times 10^3$
A	260	− 0.62	620	2.2	0.19	19.1
B	231	− 8.45	560	− 8.2	0.22	1.5
C	233	− 2.15	590	0.7	0.26	13.7
D	314	− 8.02	740	− 7.5	0.18	3.3
E	254	− 8.80	620	− 8.0	0.21	4.6
F	(664)	− 3.86				

* Values given are of the modulus of rigidity, R; Young's modulus, E; Poisson's ratio σ; and of the pressure coefficient of these moduli. Unit $= 10^3$ kg/cm^2 $= 0.9806$ kilobar.

Early investigators found that unannealed glass has smaller elasticity coefficients than annealed glass. Quincke found that Young's modulus was smaller for strained glass than for unstrained, but he gave no data. Winkelmann and Schott compared the values of Young's modulus, as determined from the velocity of sound, of strained and annealed Jena 16^{III} glass, No. 61 of Table III. 4; the values found were respectively 701.8 and 563.2. Ludwig, also working with Jena 16^{III} glass, but of slightly different composition, found values of 679.8 and 712.4 for strained and annealed samples.

The most extensive study of the effect of strain was that of Berndt,[53] who determined the effect on a number of properties. He used an optical glass (near No. 8, Table III. 4) and found Young's modulus for the strained glass to be 755, for the annealed glass 814, thus confirming the

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[53] Berndt, G., *Z. Instrumentenk.*, **40**, 20, 37, 56, 70 (1920).

conclusion that the elasticity of strained glass is less than that of glass free from strain.

Meikle[54] compared Young's modulus of the thermally toughened glass "Armourplate" with that of untreated glass of the same composition, and found the difference to be small, 780 and 759 kilobars, for sheets of "Armourplate" $\frac{1}{4}$ and $\frac{5}{16}$ inch thick, respectively, and 869 and 863 kilobars for the corresponding sheets of untreated glass.

That the effect of annealing is not only to remove mechanical strain, but also to bring the glass into a condition approximating to internal equilibrium has frequently been mentioned. Stong[49] (cf. p. 311), in a careful and precise study in which the effect of annealing in removing mechanical strain, and of heat treatment below the annealing temperature were separately considered, found that Young's modulus could be altered by about seven per cent by heat temperature, the value of the modulus increasing with decreasing temperature of heat treatment. It is not sufficient to specify "annealed glass" when reporting values of modulus of high accuracy. The complete annealing schedule must be given.

Elastic After-effect

The preceding discussion dealt with elastic effects in which the original dimensions were regained immediately on removal of the load. Indeed, every care was usually taken in the manner of loading that this should be so; the load was quickly put on, readings were taken immediately, and the load was removed, for experience has shown that even within the limit of "perfect elasticity" the time element is an important factor. Much study has been given to the phenomenon of elastic after-effect in glass. Among early workers were Weber,[55] Kohlrausch,[56] and Boltzmann,[57] while the most exhaustive investigation was that of Weidmann,[58] which was given in considerable detail by Hovestadt.[59]

The earlier experiments showed that when glass was subjected to a deforming stress, maintained for a considerable time, on removal of the stress all the strain did not immediately disappear. Weidmann defined elastic after-effect as the ratio of the deformation remaining after a given time to the original deformation. He showed that the after-effect was independent of the original deformation and also of the dimensions of the test-piece, and was determined only by the composition of the glass and the duration of loading. Further, if a light loading was

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[54] Meikle, J., *J. Soc. Glass Tech.*, **17**, 149 (1933).

[55] Weber, G. E., *Ann. Physik Chem.*, **34**, 247 (1835).

[56] Kohlrausch, F., *Ann. Physik Chem.*, **119**, 337 (1863); **128**, 1, 207, 399 (1866); **158**, 337 (1876).

[57] Boltzmann, L., *Ann. Physik Chem. Erg. Bd.* **7**, 624-654 (1875).

[58] Weidmann, G., *Ann. Physik Chem.*, **29**, 214-49 (1886).

[59] Hovestadt, H., "Jena Glass," English translation by Everett, J. D. and A., Macmillan, New York, 1902.

immediately followed by a heavy one, the after-effect showed an increase; if, however, several successive observations were made with this heavy loading, the after-effect diminished again, and after about three such loadings it resumed and retained its original magnitude. Transition from heavy to light loading gave the opposite result. The after-effect was increased by tapping the loaded glass, but diminished by tapping or warming after removal of the load. The after-effect diminished with increasing temperature.

The effect of composition was studied with a series of special glasses, and one Thuringian glass; the compositions are in Table XII.14. In carrying out the experiments, thick-walled capillary tubes were clamped at one end, further supported on a knife-edge, and the load was applied at the other end. The load was left on in all cases for ten minutes. Table XII.14 gives the elastic after-effects, in terms of the ratio of deformation remaining after a given time to the original deformation, as defined above. The outstanding conclusion drawn by Weidmann was

TABLE XII. 14—Elastic After-effect in Experimental Glasses

After Weidmann

Glass No.	Time after removal of load (seconds) 20	40	60	90	120	180	300	420	600	900	Temp. (° C.)
II	.0018	.0008	.0005	.0003							3
IV	.0011	.0006	.0004	.0003							11
V.	.0036	.0028	.0022	.0018	.0014	.0010					4
VII	.0088	.0073	.0059	.0047	.0037	.0023	.0014				3
X	.0027	.0021	.0017	.0014	.0010	.0008					4
XI	.0038	.0025	.0019	.0013	.0009	.0005					12
XIX	.0085	.0057	.0040	.0027	.0019	.0011	.0005				4
XXII	.0150	.0138	.0124	.0113	.0094	.0085	.0075		.0054	.0042	16
16^{III}	.0065	.0045	.0033	.0025	.0019	.0014					7
17^{III}	.0323	.0259	.0221	.0185	.0157	.0128	.0096	.0079	.0057	.0032	3
18^{III}	.0036	.0024	.0015	.0011	.0008	.0005					8
Thur.	.0106	.0095	.0084	.0075	.0066	.0057	.0039		.0021		1

Compositions of the above glasses

No.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	PbO	Al_2O_3	Li_2O
II	24		7			53			16	
IV	70			13.5	16.5					
V	54			16			30			
VII	51	9.3					27.7	3.7	1.8	6.5
X	46	6	8			40				
XI	65	12		18					5.	
XIX	50		15			15	20			
XXII	66		14	14	6					
16^{III}	67.5	2	14		7		7		2.5	
17^{III}	69		15	10.5					5	
18^{III}	52	9		9			30			
Thuringian	68.69		5.87	7.32	15.72				2.1	

that glasses containing both potash and soda show the largest, and those containing only one alkali show the smallest, elastic after-effect.

Phillips[60] stretched a fiber of glass for about 14 hours, and found a slow elongation, x, in magnitude proportional to the logarithm of the time, t, after the beginning of the pull, represented by the formula $x = a + b \log t$, in which a and b are constants. Reproducible results could not be obtained with freshly-drawn fibers, but were obtained with fibers which had been aged a few months. "When the load was left on for a long time and then removed the creep back was proportional to the logarithm of the time which had elapsed since the removal of the load if the duration of the observations was short compared with the time since the load was put on."

Borchard[61] found an elastic after-effect in which the strain increased as a logarithmic function of the time. It was independent of the amount of deformation and the dimensions of the sample, and was independent of the method of producing the deformation. The elastic after-effect became smaller with increasing temperature and was increased by vibration. Vibration after removal of the stress increased the rate of recovery from the deformation.

The experiments of Spencer[62] give conclusive evidence of recovery from deformation. He wrapped fibers of glass, of percentage composition: SiO_2, 63; Na_2O, 9; K_2O, 6; PbO, 22 around a cylinder two centimeters in diameter, and held them for months. On cutting the fibers loose they immediately opened out to coils of about 60 centimeters in diameter, and seemed to have acquired a "permanent set." They were left floating on mercury, and they gradually diminished in curvature, but after five years they were still slightly curved.

The experimental evidence is not unanimous as to creeping of glass under load. No evidence of creep before breaking was found by Grenet (p. 336). Experiments by J. T. Littleton, cited by Preston, made with strong rods of a borosilicate glass, using high stresses and delicate optical tests, gave no evidence of creep; nor did experiments by G. A. McKee, also cited by Preston, in which laths of glass were subjected to cross-bending for from four to fifteen hours. The observed differences in behavior may result from differences in the compositions of the glasses used, or from differences in the manner of carrying out the experiments; or other uncontrolled factors may be important.

Similar results have been obtained in studying the "thermal after-effect," a phenomenon which probably is the result of the same causes as the elastic after-effect. A newly-made thermometer slowly contracts

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[60] Phillips, P., *Phil. Mag.*, 9, 520 (1905).

[61] Borchard, K. H., *Sprechsaal*, 67, 297 (1934).

[62] Spencer, C. D., "Discussion of the flow of glass subjected to stress," presented at the Annual Meeting, American Ceramic Society, February, 1931. Not published; details are quoted from Preston, F. W., *J. Am. Ceram. Soc.*, 18, 220 (1935).

at ordinary temperatures, causing the ice-point to rise slowly, an effect known as the "secular rise of the zero." This creeping-up of the ice-point can be interrupted by raising the temperature of the thermometer to 100° C. and cooling it quickly; the lowering of the ice-point so produced is the "depression constant." On being left in ice the zero again rises, and the rate of recovery, as well as the depression constant, is dependent on the composition of the glass.

The thermal after-effect was discussed at length by Hovestadt[59] on the basis of experiments by Weber[63] and by Wiebe.[64] The studies of Wiebe, made in collaboration with Schott, considered the depression-constant as well as the speed of recovery, permanence of zero and suitability for blowpipe working, and resulted in the selection of the "normal thermometer glass," 16^{III}, and the "borosilicate thermometer glass," 59^{III}. They also found that glasses containing both Na_2O and K_2O gave large depression constants, and that the best glasses contained only one alkali. The correlation between elastic and thermal after-effects was made by Weidmann, who said, "There is a relation between the elastic and thermal after-effects, and a thermally good glass is also good elastically, while a thermally poor glass is poor elastically."

Mueller[65] gives the following depression constants, in ° C., for standard thermometer glasses: Verre dur, 0.07 to 0.11; "Kew glass," 0.20; normal thermometer (Jena 16^{III} or Corning 881), 0.04 to 0.08; borosilicate thermometer (Jena 59^{III} or Corning 880), 0.03 to 0.04; Jena 1565^{III}, 0.01; Jena combustion, 0.03.

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[63] Weber, R., *Sitzber. k. preuss. Akad. Wiss.*, Dec. 13, 1883.

[64] Wiebe, H. F. W., *Sitzber. k. preuss. Akad. Wiss.*, July 17, 1884; Nov. 12, 1885. *Zeit. Instrumentenk.*, **6**, 167 (1886).

[65] Mueller, E. F., *Int. Critical Tables*, **1**, 55 (1926).

Chapter XIII

The Strength of Glass

When glass is subjected for short periods to stresses within the limits of elasticity, the resulting strain disappears after the removal of the stress, and the piece returns to its original dimensions. With most substances, on addition of load beyond the elastic limit, a condition is reached in which yielding takes place continuously, and if the load is maintained, fracture results. The substance in which there is an initial elastic limit, that is, which is not viscous, is said to be in a condition of plasticity in the region beyond the elastic limit in which deformation takes place continuously. With glass, there appears to be no region of plasticity, and Hooke's law holds up to the breaking point of the glass. There is no accepted relation between the elasticity of a substance and its ultimate strength. A high value of Young's modulus does not necessarily imply a large tensile strength, nor does a high modulus of compressibility imply a large crushing strength. Also, glass may be broken in any one of many different ways, by tension, compression, twisting, or impact; but there is no connection between the numerical values of the breaking strengths as determined by these several methods. Indeed, it is probable that in all the various methods of applying stress to glass, fracture always takes place in tension. A failure in uniform compression is unthinkable, and fracture results from tensile stresses developed by the manner of applying the load.

There is no consensus of opinion as to the conditions under which a body is ruptured. It has been assumed that rupture takes place when a maximum tension is reached; or when a maximum extension is reached; or when the difference between the greatest and least stresses reaches a maximum value. Love [1] summarized evidence tending to disprove each of these hypotheses, but did not attempt to replace them. The work of Griffith [2] on glass, and of Joffe [3] on crystals makes probable the hypothesis that since the true ultimate strength in tension is that determined by the molecular cohesion the far lower values found in practice are caused by surface scratches or flaws. Griffith assumed that the molecules in the glass orient themselves in groups such that in certain directions the

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[1] Love, A. E. H., "The Mathematical Theory of Elasticity," 119, 2nd ed., Cambridge Univ. Press, 1906.

[2] Griffith, A. A., *Trans. Roy. Soc. (London), A*, **221**, 162 (1920).

[3] Joffe, A. F., "The Physics of Crystals," McGraw-Hill, New York, 1928. See also Zwicky, F., *Proc. Natl. Acad. Sci. U. S.*, **15**, 253 (1929).

attractive forces are minimum, and that such groupings are incipient flaws. Other writers have emphasized the importance of flaws and surface scratches, but the usual conception of such imperfections is less hypothetical than that of Griffith.

Griffith proposed a theory of the fracture of glass based on the "theorem of minimum energy," according to which the equilibrium state of a body deformed by surface forces is such that the potential energy of the whole system is a minimum. "The new criterion of rupture is obtained by adding to this theorem the statement that the equilibrium position, if equilibrium is possible, must be one in which rupture has occurred if the system can pass from the unbroken to the broken condition by a process involving a continuous decrease in potential energy." Rupture thus involves the formation of a new surface, with a concomitant increase in surface energy; and mathematical analysis of the case of a rupture proceeding from a crack leads to the expression for the breaking stress, R,

$$R = \sqrt{\frac{2ET}{\pi \sigma c}}$$

in which E is Young's modulus, T, the surface tension, σ, Poisson's ratio, and c the half length of the crack. A test of this expression, using glass bulbs and tubes, gave a mean value of $R\ c$ of 239, with a maximum of 251, while the value calculated from the experimentally determined values of E and T was 266. Calculation of the maximum stress at the end of the crack indicated that the maximum strength of the glass was of the order of 200 kilobars. This value is of the same order as that calculated from the "intrinsic pressure" or molecular cohesion, and values of the same order were found in tensile tests on fibers.

The theoretical treatment of Polanyi[4] is frequently reproduced. If it is assumed that the elastic energy stored in a rod at the moment of breaking is all transformed into the energy of the two new surfaces formed, then $1/2(Fd) = 2\gamma$; and if it is further assumed that Hooke's law holds up to the breaking point, $F^2 = 4E/a$; in which F is the breaking stress, E Young's modulus, d the extension at the breaking point of a length equal to the intermolecular distance, a, and γ the surface tension. It will be observed that the introduction of the quantity a involves a further unverifiable assumption. Also, the surface tension is that at the interface glass:air at ordinary temperatures, and the extrapolation of surface tension from the temperature at which it can be measured to room temperature is without justification. No method has been devised for measuring the surface tension at the interface solid:air.

[4] Polanyi, M., *Z. Physik*, **7**, 323 (1921).

Other methods for calculating the theoretical strength of glass have been proposed. Born and Landé[5] and Joffe[3] based their discussion on the electric forces in a crystal lattice. Andrade[6] discussed Polanyi's method and a method based on the periodic variation of shearing stresses in a crystal, and in addition gave an illuminating discussion of the problem of ultimate strength. The methods which have been proposed are far from satisfactory, and are in contradiction to each other and to experiment. Until great advance is made over our present knowledge the calculation of the theoretical strength of glass is even more uncertain than is the measurement of the strength, and suffers from the fault that the necessary underlying assumptions are usually so obscured by mathematics as to lend to the calculation an appearance of finality wholly unjustified by the facts.

The strength of a great number of glass samples has been measured, but much uncertainty exists as to the significance of the results. Most of the data have been obtained with glass of unknown composition. Results of a satisfactory degree of concordance have rarely been obtained, probably because of the effect of surface scratches, as pointed out by Griffith[2] and by Littleton.[7] It has been shown by Inglis[8] that stresses are increased around an elliptical discontinuity by twice the eccentricity of the ellipse; consequently surface scratches will determine the point of fracture and greatly reduce the apparent strength. Brodmann[9] increased the strength of glass by etching off the surface with hydrofluoric acid, thus rounding out angular discontinuities. Griffith avoided the difficulties arising from surface flaws by using freshly drawn fine filaments. Littleton has devised a method for eliminating the surface effects in the determination of the tensile strength of glass by using a chilled specimen, whose surface is under strong compression. Since glass is much stronger in compression than in tension, when the load is applied, the interior layers, already under tension, reach their ultimate strength before the surface layers. The actual tensile strength is obtained by combining graphically the original stress, as determined from the strain pattern obtained in polarized light, with the load stress. Both Griffith and Littleton obtained much higher results than previous investigators, and it would seem probable that in most of the work recorded in the literature the results served to measure only the surface condition of the glass.

Murgatroyd[10] cited experiments indicating that when scratches, produced with a diamond having a 130° angle, had a width only of the

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[5] Born, M., and Landé, A., *Ber. deut. physik. Ges.*, **20**, 210 (1918).

[6] Andrade, E. N. da C., *Science Progress*, **120**, April (1936).

[7] Littleton, J. T., *Phys. Rev. (2)*, **22**, 510 (1923).

[8] Inglis, *Proc. Inst. Naval Architects*, March 14 (1923).

[9] Brodmann, C., *Nachr. kgl. Ges. Wiss. Göttingen*, **44**, 1894.

[10] Murgatroyd, J. B., *J. Soc. Glass Tech.*, **17**, 260 (1933).

order of 5×10^{-4} cm., the effect on thermal endurance was negligible, but that with larger scratches the effect became apparent. Both Murgatroyd and Preston[11] considered that the probability of the occurrence of scratches, which increases with increasing diameter and length of the sample, is an important factor.

Preston[11] carried further the conception that the strength commonly measured is chiefly that of the surface by making the assumption that "strength" is directly proportional to cross-section area and inversely proportional to the perimeter. This led to the equation $W = j D$, in which W is the load carried, D the diameter, j, a quantity called "surface strength," having the dimensions of a force per unit length, which are those of a surface tension. An examination of the results of Griffith on fibers showed a smaller range of values for j than for "breaking strength" in the ratio of 1:12, and a discussion of the fracture produced by a steel ball pressed on a disc likewise indicated the probability that such a physical quantity as j determines the strength of the glass.

Milligan[12] found that the strength of glass containing cracks was greatly influenced by the medium in contact with the glass surface. Exposure to air saturated with water or alcohol considerably reduced the strength. Moistening the crack with water reduced the strength about 20 per cent, and dry paraffin oil increased the strength by the same amount. An increased strength was observed in glass which had been dried after wetting with water, and a larger increase in strength, about 20 per cent, when the glass was dried after wetting with a dilute solution of sodium silicate. Milligan did not advance an explanation of the effects, but did point out that explanations based on the difference in the surface tensions in the various cases required more knowledge than exists at present in regard to the surface energies involved. Such hypotheses fail to explain the increase in strength obtained with oil, as well as the fact that wetting with water produced no observable effect on the strain relations around the crack.

When a test-piece under tension is broken under such conditions that the initial fracture occurs in the interior, it is probable that the result represents the true tensile strength of the glass, or at least is not affected by surface flaws. Gehlhoff and Thomas[13] assumed that the "mirror" part of a fractured surface represented a flaw, and corrected their results by an arbitrary assumption of 10 per cent of mirror area in the fractured surface. Müller[14] further developed the thesis that the mirror area represents a flaw, and is to be neglected, and calculated a "mirror-free"

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[11] Preston, F. W., *J. Soc. Glass Tech.*, **17**, 4 (1933).
[12] Milligan, L. H., *J. Soc. Glass Tech.*, **13**, 351 (1929).
[13] Gehlhoff, G., and Thomas, M., *Z. tech. Physik*, **7**, 105 (1926).
[14] Müller, K. H. H., *Z. Physik*, **69**, 431 (1931).

strength from the formula $Z = Z_0\left(1 - \frac{s}{q}\right)$ in which Z is the observed tensile strength, the breaking load divided by the total area, q; Z_0 the "mirror-free" breaking strength, considered to be a true constant of the material; and s the area of mirror fracture.* With rods of thickness ranging from about 2.5 to 4 mm., Z_0 showed a closer approach to constancy than Z. Preston and Littleton[15] questioned the validity of the above treatment, and said: "Perhaps it might be well to add here that some authors have taken this fissure theory somewhat extravagantly. The fissure or flaw is essentially a microscopic or sub-microscopic object, and should not be confused with the whole area of the polished-appearing zone that surrounds it after the fracture is completed. Thus Gehlhoff and Thomas should not have corrected their results by a factor to allow for the area of this polished zone. This polished zone is simply that part of the advancing fracture that travelled comparatively slowly."

The studies of Preston[16] on the rupture of glass are helpful in the interpretation of the fracture surfaces. He stressed the fact that the head of an advancing fissure endeavors to maintain its direction at right angles to the principal tension at its advancing head. "A smooth, bright (polished) fracture indicates that the parting of the glass is not violent—contraction flaws that form slowly have bright clear fractures—whilst the hackly fracture indicates a more sudden shock. The coarser the hackle the more violent and sudden was the parting of the glass."

The preceding discussion has referred chiefly to the tensile strength of glass. Compressive strength refers to the destruction of the specimen by a unidirectional thrust, which produces both a compression and a shear. Failure under uniform compression is difficult to conceive, and would require stresses sufficient to affect the fundamental atomic forces. In compression tests the material actually breaks in tension, either that resulting from the normal stress distribution or that developed in the surfaces to which the load is applied.

The manner of applying the load is important. When the press is set up with precision, and the surfaces are accurately ground, greater strength is obtained with bearing surfaces of harder metals. Softer metals flow parallel to the surface of the glass, causing a tearing action. In commercial practice, however, it is not usually practicable to use a ground and polished surface contact. In this case the hardened metals tend to localize the pressures on their points of contact, and hence the softer metals are found to give better results. The soft metals flow, and thus equalize the distribution of pressure.

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* Cf. Apelt, p. 336.

[15] Preston, F. W., and Littleton, J. T., *J. Soc. Glass Tech.*, **13**, 336 (1929).

[16] Preston, F. W., *J. Soc. Glass Tech.*, **10**, 234 (1926); *J. Am. Ceram. Soc.*, **9**, 654 (1926); *J. Am. Ceram. Soc.*, **14**, 419 (1931).

Definitions and Units

The usual methods of loading a test-piece to destruction lead to definitions of tensile, crushing, and bending strength. The tensile and crushing strengths are each defined as the stress per unit area at the destruction limit. The bending strength is usually stated in terms of the modulus of rupture, B, which for the case of a rectangular bar of width b, height h, resting on two parallel edges a distance l apart and loaded at the middle point by a force p becomes $B = \frac{3pl}{2bh^2}$, and for a rod of circular cross-section becomes $B = \frac{pl}{r^2}$, in which r is radius of circular cross-section.

The strength of glass is a stress intensity, which in practice is usually expressed as mass per unit area, the mass being used as a unit of force. The dimensions of the number giving the strength of glass are accordingly the same as those of a modulus of elasticity, as are also the conversion factors. These are given in Table XII. 2. In the following tables and discussions the unit commonly used is the same as that used in the discussion of elasticity, namely, the bar.

One-Component Glasses

Of the various pure oxides that can be obtained in the glassy state, only silica has been measured for its mechanical strength. The data in the literature have been discussed by Sosman,[17] and summarized as shown in Table XIII. 1. The tensile strength given here is that of fibers, and is much greater than the usual values for strength of larger samples.

TABLE XIII. 1—Strength of Silica Glass
(*After Sosman*)

	Tensile Strength (Bars)	Crushing Strength (Bars)	Bending Strength (Bars)
Strength usually to be expected in small specimens	3 to 8	19.5	
Maximum observed	11.5	22.6	0.675

Two- and Three-Component Glasses

The only systematic experiments on the strength of glasses as a function of the composition are those of Gehlhoff and Thomas, discussed in detail below. The strengths of a few other two- and three-component glasses are included in the tables under multi-component glasses, but they represent incidental, not systematic, determinations.

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[17] Sosman, R. B., "The Properties of Silica," Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

Gehlhoff and Thomas[13] made an extensive series of measurements on glasses derived from the two-component glass 0.18 Na_2O, 0.82 SiO_2, by replacement of SiO_2 by CaO, B_2O_3, BaO, Al_2O_3, PbO, K_2O, Na_2O, (SiO_2, MgO, ZnO, Fe_2O_3); the order given is that of decreasing effect on the tensile strength, and the oxides in parentheses had but little effect. This order does not agree with that of Winkelmann and Schott. The results are summarized in Fig. XIII. 1. In general, the initial effect of any of the substituting oxides was to increase the tensile strength. The oxides included in the parentheses above had little effect, and it is not certain that there was a real diminution in strength. Also, several of the curves rise to a maximum, then fall; continued addition of any of these oxides results first in an increase, then in a diminution of strength.

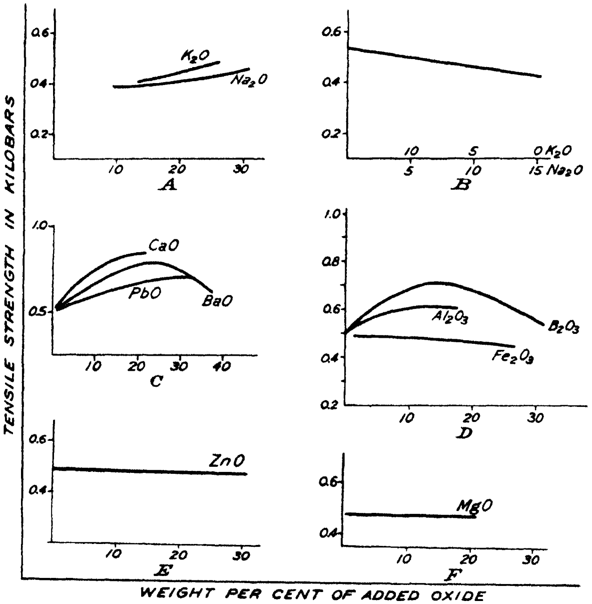

FIGURE XIII. 1.—Tensile Strength of Experimental Glasses. After Gehlhoff and Thomas.

Measurements of bending strength were made by supporting the test rods on knife edges 10 cm. apart, and applying the load by adding mercury to a receiver hung from a third central knife edge. The rods were always elliptical in cross-section, and the bending strength was calculated from the formula $F = (P.l)/(a^2b)$, in which F is the bending strength, l is the distance between supports, a and b are the major and minor axes of the ellipse, and P is the load. The results are summarized in Fig.

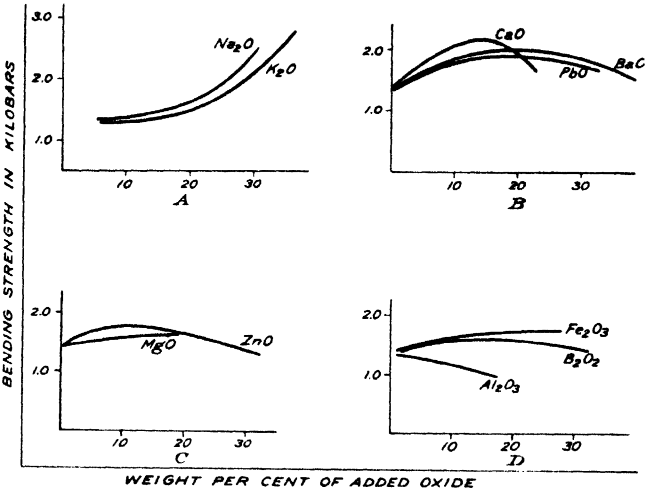

FIGURE XIII. 2.—Bending Strength of Experimental Glasses. After Gehlhoff and Thomas.

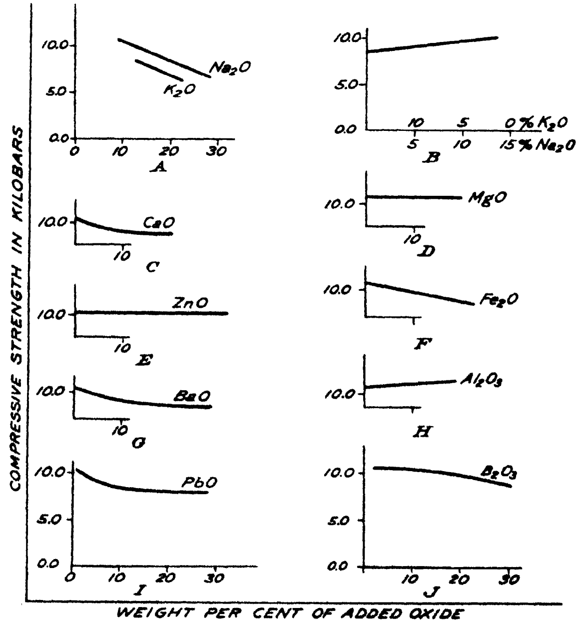

FIGURE XIII. 3.—Crushing Strength of Experimental Glasses. After Gehlhoff and Thomas.

XIII. 2. The order of the oxides in respect to their effect on the bending strength is: CaO, BaO, ZnO, MgO, B_2O_3, SiO_2, Al_2O_3. The alkalies have little effect in small amount, but the curves are strongly concave upward, and the bending strength at 30 per cent alkali is almost twice that at 10 per cent. Greene* pointed out that the formula used by Gehlhoff and Thomas was in error, a factor of 8 in the numerator being omitted, and that the values obtained by them for bending strength should be multiplied by 8.

Measurements of crushing strength were made with polished glass plates 1.5 to 2 mm. thick, and about 4 mm. square. Even with the most careful adjustment of the apparatus the results often varied 15 per cent from the mean, and as a rule the variation was 5 per cent. The results are summarized in Fig. XIII. 3. The alkali oxides have the greatest effect in diminishing the crushing strength, and there is no relation between the observed crushing strength and the tensile strength. The order found for the oxides is: Al_2O_3, (SiO_2, MgO, ZnO), B_2O_3, Fe_2O_3, (BaO, CaO, PbO), Na_2O, K_2O, the oxides in parentheses having about the same effect.

Multi-component Glasses

Little systematic information exists as to the effect of chemical composition on the strength of glass. The early experiments of von Kowalski [18] were made on glass of unspecified composition, and serve only to give a possible order of magnitude. The work of Winkelmann and Schott [19] was more comprehensive, and included determinations of tensile and comprehensive strength of a number of the same glasses discussed under elasticity; their values for the tensile and compressive strength are included in Table I. 2. The value given for the tensile strength represents the maximum obtained; the minimum values were from 4 to 22 per cent lower. Winkelmann and Schott gave factors for calculating tensile and compressive strength from chemical composition. The calculated strengths agreed with the observed ones to within about the same percentage error as the observations agreed among themselves, that is, to about 20 per cent, but did not agree with the results of other observers.

Some additional determinations of the compressive strength of a few Schott glasses made by Föppl [20] are included in Table I. 2; the determinations were fewer and less concordant than those of Winkelmann and Schott.

* Greene, C. H., *J. Am. Ceram. Soc.*, **15**, 59 (1932).

[18] Kowalski, J. v., *Ann. Physik Chem.*, **36**, 307 (1889); **39**, 155 (1890).

[19] Winkelmann, A., and Schott, O., *Ann. Physik Chem.*, **51**, 697 (1894).

[20] Föppl, A., *Sitzber, math.-physik. Klasse Akad. Wiss. München*, **3**, 505 (1911); abstract in *Z. Instrumentenk.*, **32**, 211 (1912).

Williams[21] made an extensive study of the transverse strength of 5000 samples of glass used for glazing purposes, on strips 18 × 2 inches, using a 16-inch span, and gave the following values: single or double strength window glass and 26-oz. clear sheet glass, 0.48 kilobar (7000 pounds per sq. in.); 29 to 39-oz. or $\frac{3}{16}$-in. clear sheet or $\frac{1}{4}$-in. plate, or rolled sheet and wire glass, 0.45 kilobar (6500 pounds per sq. in.).

Holland and Turner[22] made tests on specimens 10 cm. long (effective length between knife edges 7.6 cm.), and 0.4 to 1.2 cm. wide, cut from 14-oz. flat drawn sheet glass, with the length of the specimen at right angles to the direction of drawing. The specimens tested either had their sides (1) ground and polished, (2) ground, polished, and fire-polished, or (3) had their diamond-cut edges in tension. The characteristic fracture was V-shaped. The results could be represented by the equation strength (kg./cm.^{2}) $= c + m/d$, in which c and m are constants, and d is the width of the specimen in centimeters. Values of the constants were: (1), $c = 480$, $m = 67$; (2) 766 and 219; (3) 451 and 89.

TABLE XIII. 2—Properties of Some Miscellaneous Glasses

After Lecrenier

No.	SiO_2	Na_2O	K_2O	CaO	PbO	Al_2O_3 Fe_2O_3	Density	Tensile Strength in Kilobars	Crushing Strength in Kilobars	Auerbach Hardness	Volume (cc.) removed by 1 min. grinding
1	55.20		9.92		34.81	0.25	3.227	0.581	8.36	265	1.696
2	49.17		9.39		41.17	0.25	3.342	0.544	7.93	262	1.593
3	58.35	7.87	3.91		29.42	0.30	3.006	0.606	8.49	233	1.301
4	61.74	7.40	1.38	3.73	25.00	0.60	2.971	0.694	8.78	202	1.069
5[a]	61.00	11.24				0.60	2.876	0.692	7.58	231	0.964
6	71.66	13.85		11.48	2.41	0.50	2.541	0.890	8.98	133	0.933
7	67.91		20.52	10.82		0.60	2.497	0.918	8.57	243	0.888
8	72.04	17.02		10.19		0.60	2.521	0.870	8.99	134	0.854
9	73.08	15.84		10.33		0.60	2.504	0.880	9.11	141	0.794
10	72.19	15.62		11.38		0.50	2.547	0.896	9.02	130	0.754
11	73.26	14.43		11.71		0.45	2.513	0.905	9.14	131	0.733
12[b]	68.43	15.83	3.40	8.03		0.65	2.503	0.802	8.77	226	0.544

[a] Contains 29.61% BaO [b] Contains 2.51% B_2O_3.
In addition each glass contained about 0.15% As_2O_3

Lecrenier[23] determined the tensile and compressive strength of the glasses of Table XIII. 2. No information was given as to the degree of concordance of the observations.

The method devised by Littleton[24] for diminishing the effect of scratches has already been mentioned. The tests were made on a bar of glass, cut from the middle of a slab which had been treated in such a way as to leave the upper and lower surfaces of the bar under high compression, while the inside was in tension. When such a bar was

[21] Williams, A. E., *J. Am. Ceram. Soc.*, **6**, 980 (1923).

[22] Holland, A. J., and Turner, W. E. S., *J. Soc. Glass Tech.*, **20**, 72 (1936).

[23] Lecrenier, A., quoted by Le Chatelier, H., "Kieselsaure und Silicate," 246, Leipzig, 1920.

[24] Littleton, J. T., *Phys. Rev.*, **22**, 510 (1923).

broken by bending, the tension introduced in the lower surface was largely neutralized by the initial compression, so that the maximum tension was not in the lower surface, but in a zone nearer the neutral axis. The actual tensile strength was obtained by combining graphically the original stress, as determined from the strain pattern obtained in polarized light, with the load stress. Table XIII. 3 gives the results obtained by Littleton with two glasses, a borosilicate and a lead glass.

TABLE XIII. 3—The Strength of Glass by Littleton's Method

Borosilicate			Lead Glass		
Annealed Tensile Strength (Kilobars)	Strained		Annealed Tensile Strength (Kilobars)	Strained	
	Initial Compression	Tensile Strength (Kilobars)		Initial Compression	Tensile Strength (Kilobars)
1.052	0.844	1.392	0.667	1.176	1.329
0.573	1.010	1.628	0.744	1.098	1.314
0.692	0.863	1.412	0.814	0.991	1.216
0.755	1.154	1.418	0.559	1.077	1.206
0.585	0.954	1.405	0.537	1.356	1.363
0.706	0.832	1.188	0.705	1.274	1.172
0.612	1.039	1.377	0.751	1.246	1.098
0.717	1.050	1.637	0.849	1.113	1.094
0.630	0.982	1.520	0.688	1.283	1.051
0.767	0.852	1.439	1.185	0.952	1.138
Mean					
0.706	0.977	1.445	0.747		1.198
Mean deviation from the mean					
13.3%		6.20%	16.0%		7.3%

By making the tests in this manner, the concordance of the results is greatly increased, as shown by the smaller value of the mean variation from the mean, and the tensile strength is about doubled. The higher the initial compression the higher the value of the tensile strength obtained, and it is probable that even these results do not represent the true tensile strength of glass free from the effect of surface imperfections.

Gooding[25] measured the tensile strength of glass of the percentage composition: SiO_2, 73.80; Na_2O, 16.00; MgO, 0.09; CaO, 8.85; Al_2O_3, 0.75; Fe_2O_3, 0.04. The specimens were rods, approximately 1 mm. in diameter, with constrictions in their middle portions; these constrictions were made by heating under load. The type of fracture obtained depended on the observed strength; a fracture surface which was largely smooth was associated with a lower value of tensile strength than one which was rough. The most common type of break (observed in 60 to 70 per cent of the specimens) was described as: "one edge very rough, the rest smooth, giving the appearance of a 'castle on a hill.' Between

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[25] Gooding, E. J., *J. Soc. Glass Tech.*, **16**, 145 (1932).

the very rough and smooth sections is a narrow zone of smaller 'hackle.'" The strength was found to increase with decreasing diameter, an effect similar to that observed by Griffith with smaller fibers. Acid polishing and matt etching considerably increased the strength. The strength did not appear to be affected by the presence of sulfurous acid fumes during annealing, by the temperature at which the constriction was made, or by different loading methods.

Strength of Fibers

Griffith[26] studied the tensile strength of fibers of the composition SiO_2, 69.2; K_2O, 12.0; Na_2O, 0.9; Al_2O_3, 11.8; CaO, 4.5; MnO, 0.9, and found that it was affected (1) by the maximum temperature to which the glass was heated before drawing the fibers, the best results being obtained when the glass was heated to from 1400° to 1500°; (2) by the temperature during drawing of the fibers, low results being obtained when the fiber was allowed to get too cold; and (3) by the age of the fiber, strengths as high as from 15.2 to 62 kilobars having been observed in fibers up to 0.5 mm. in diameter within a few seconds after preparation. The amount of stress was computed from the angle to which the fibers could be bent before breaking. The strength diminished with time, reaching a steady state after a few hours. The experiments listed in Table XIII. 4 were made on fibers which had been aged 40 hours. Results of the same order of magnitude were obtained in experiments on cracked bulbs and plates.

Table XIII. 4—Strength of Glass Fibers

After Griffith

Diameter (mm.)	Tensile Strength (Kilobars)	Diameter (mm.)	Tensile Strength (Kilobars)
1.016	1.715	0.0241	8.053
0.1067	2.912	0.0191	9.227
0.0706	3.498	0.0178	11.295
0.0571	4.413	0.0152	12.72
0.0508	5.480	0.0142	10.60
0.0470	6.094	0.0127	13.41
0.0444	5.688	0.0097	15.98
0.0355	5.868	0.0066	22.83
0.0335	6.850	0.00418	34.30
0.0292	6.109	0.00330	33.83

Onnes and Braak[27] determined the tensile strength of fibers of Thuringian glass, of unknown composition, at ordinary temperature and in liquid air. Their results are assembled in Table XIII. 5. The annealed fibers showed a slight decrease in strength, and the low-tem-

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[26] Griffith, A. A., *Trans. Roy. Soc. (London)*, *A*, 221, 163 (1920).

[27] Onnes, H. K., and Braak, C., *Verslag. Akad. Wetenschappen (Amsterdam)*, 16, 890 (1907-8).

perature tests showed a marked increase in strength. The interpretation of this latter fact is uncertain because of the fibers having been immersed in liquid air, and it is possible that liquid air tended to increase the strength in the same manner that Milligan found dry paraffin oil to increase the strength of glass. Onnes and Braak mentioned the difference in appearance between the fracture at ordinary temperature and in liquid air. The order of magnitude of their results agreed with those of Griffith for fibers within the same range of diameters, but there was no tendency in Onnes and Braak's results toward an increase of strength with decreasing diameter, the outstanding feature of Griffith's results.

TABLE XIII. 5—Strength of Glass Fibers

After Onnes and Braak

Load (grams)	Diameter (mm.)	Tensile Strength (Kilobars)	Load (grams)	Diameter (mm.)	Tensile Strength (Kilobars)
		Unannealed fibers			
257.6	0.119	2.26	2615	0.424	1.80
496.5	0.192	1.72	2785	0.446	1.74
457.8	0.384	1.24	1425	0.351	1.44
2325	0.384	1.94	1635	0.370	1.72
1175	0.257	2.22	1325	0.325	1.57
1475	0.325	1.73	1555	0.298	2.21
1695	0.311	2.20	2335	0.370	2.11
4105	0.487	217	Mean		1.936
			Mean deviation		12.6%
		Annealed fibers			
2920	0.438	1.90	1910	0.325	2.29
3530	0.597	1.23	1760	0.322	2.12
2120	0.532	0.94	2850	0.445	1.80
			Mean		1.715
			Mean deviation		25%
		Fibers at liquid air temperature			
1993	0.280	3.18	2498	0.297	3.52
2653	0.372	2.38	2055	0.286	3.13
2523	0.290	3.75	3550	0.359	3.44
1293	0.236	2.89	3865	0.396	3.07
			Mean		3.17
			Mean deviation		10%

Strength of Glass Tubes

In addition to the above, a number of experiments have been made on the bursting strength of glass tubes. Among those who have determined such bursting strengths are Heydweiller,[28] Schott and Hersch-

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[28] Heydweiller, A., *Ann. Physik Chem.*, **84**, 725-34 (1898).

TABLE XIII. 6—Bursting Strength of Glass Tubes

After Onnes and Braak

Diameters				
External 2R (mm.)	Internal 2R' (mm.)	$n = R/R'$	Bursting Pressure (Kilobars)	Maximum Fiber Stress (Kilobars)
	Series 1.	*Thick-walled tubes of large diameter*		
9.3	3.5	2.66	0.344	0.527
8.8	4.0	2.20	0.284	0.481
8.7	4.2	2.07	0.233	0.413
9.4	3.2	2.94	0.274	0.402
9.2	3.0	3.07	0.385	0.559
9.7	4.2	2.31	0.375	0.618
10.4	4.0	2.60	0.243	0.375
12.8	5.8	2.21	0.263	0.445
17.6	5.0	3.52	0.294	0.411
			Mean	0.470
			Mean deviation	14.4%
	Series 2.	*Capillary tubes*		
7.4	1.0	7.40	0.515	0.661
6.8	1.0	6.80	0.425	0.546
7.2	0.27	27.78	0.466	0.581
6.5	0.35	18.57	0.507	0.633
6.7	0.24	27.92	0.547	0.654
6.7	0.24	27.92	0.810	1.012
6.7	0.24	27.92	1.115	1.392
6.7	1.08	6.20	0.537	0.694
5.9	0.70	8.43	0.689	0.876
5.8	0.46	12.81	1.213	1.530
5.0	0.62	9.52	0.831	1.053
5.3	0.46	11.52	0.932	1.173
5.5	0.46	11.96	1.074	1.370
6.6	1.00	6.60	0.668	0.861
7.2	1.40	5.14	0.527	0.693
6.4	1.35	4.74	0.527	0.699
			Mean	0.902
			Mean deviation	27%
	Series 3.	*Thin-walled tubes of large bore*		
3.8	3.42	1.57	0.287	0.698
5.6	4.00	1.40	0.195	0.695
6.4	4.78	1.34	0.224	0.769
6.9	3.91	1.76	0.333	0.692
7.4	5.11	1.45	0.181	0.511
7.9	5.46	1.45	0.159	0.448
3.5	2.26	1.54	0.264	0.665
6.8	5.13	1.32	0.206	0.737
7.4	5.19	1.43	0.204	0.592
6.8	5.78	1.18	0.067	0.376
3.8	2.42	1.57	0.382	0.931
3.8	2.50	1.52	0.281	0.721
6.0	4.37	1.37	0.181	0.584
6.8	4.37	1.37	0.171	0.523
7.3	5.62	1.30	0.110	0.414
7.8	7.31	1.067	0.055	0.745
6.8	5.17	1.31	0.161	0.590
			Mean	0.628
			Mean deviation	19.6%

kowitsch,[29] Bradley and Browne,[30] Onnes and Braak,[31] and Roebuck.[32] None of these gave the composition of the glass used, and as the experiments of Onnes and Braak were more extensive than any others, and agree with the others in order of magnitude of the bursting strength, they are given in detail in Table XIII. 6.

The glass used was described as an ordinary Thuringian glass, and was the same as was used for the tensile tests on fibers mentioned above. Three groups of experiments were made: (1) with thick-walled tubes; (2) with thick-walled tubes of small internal diameter, *i.e.*, capillary tubes; and (3) with thin-walled tubes of large bore. The data were reduced to a comparable basis by calculating the maximum fiber stresses from the formula

$$T_m = \tfrac{1}{4}\left[5P_m + \left(7\frac{P_m - 1}{n^2 - 1}\right) - 1\right],$$

in which T_m is the maximum fiber stress, P_m is the bursting pressure, and n is the ratio of external to internal radius, R/R'. In deriving this formula, Poisson's ratio was assumed to be 0.25. It will be observed that the results were irregular, and that in no case did the maximum fiber stress approximately equal the tensile strength found by Onnes and Braak for fibers. (Table XIII. 5.)

Wartenberg[33] tested a Thuringian glass and three Schott glasses, "Supremax," "Durax," and "Gerateglas 20," of varying diameter, wall thickness 0.9 to 1.0 mm. The relation used to calculate fiber stress (T) from bursting pressure (P) and from outer and inner radii (r_a and r_i) was:

$$P = T\frac{[r_a^2 - r_i^2]}{[r_a^2 + r_i^2]}.$$

The maximum fiber stress (T) should have been independent of r, but there was a marked variation, different for Supremax and Duran. Average values of T at 20° in kg./cm.^{2} for tubes 10 to 25 mm. in diameter were: Supremax, 500 ± 30; Duran, 650 ± 30; Geräte ± 30; Thuringian, 480 ± 50. When Supremax was etched or was scratched with corundum, the strength was unaltered; but diamond scratches caused breaking. The form of the fused end was without influence.

Effect of Strain on the Strength of Glass

If the ordinary experiments on the breaking strength of glass measure "not the strength of glass, but the weakness of the surface,"[34] any

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[29] Schott, O., and Herschkowitsch, M., *Z. Ver. deut. Ing.*, **45**, 339-43 (1901).

[30] Bradley, W. P., and Browne, A. W.. *J. Phys. Chem.*, **8**, 37-55 (1904).

[31] Onnes, H. K., and Braak, C., *Verhandel. Akad. Wetenschappen Amsterdam, Afdeel. Natuurkunde*, **16**, 890-97 (1907-8).

[32] Roebuck, J. R., *Phys. Rev.*, **28**, 264-76 (1909).

[33] Wartenberg, H. v., Greiner, B., Tabacznik, Z., Janeszewski, D., and Krawutschke, A., *Z. tech. Physik*, **13**, 479 (1932).

[34] Quoted from Littleton, J. T., by Preston, F. W., *J. Soc. Glass Tech.*, **17**, 4 (1933).

method of improving the condition of the surface should increase the strength. This was the basis of Littleton's method for measuring the strength of glass; and was the explanation of the results of Schott[35] on compound and on thermally toughened glass. The same hypothesis explains the "toughened" glass developed in recent years, and most extensively used for automobile windshields, especially in Europe. The effect of strain on the strength of glass has been studied by several observers.

The work of Berndt[36] was done primarily to determine the effect of strain on the properties of glass. His first experiments were made on compressive strength, using a plate glass of unspecified composition and a borosilicate crown, near No. 4, Table III. 4. The strained glass was found to be about seven per cent stronger. Later experiments, using the same borosilicate crown, were more extensive. In these, pieces of glass prepared in two different ways were used. The first samples were made by sawing from a slab, in which the strain was about 50 mμ, but the sawed test strip was found to have a strain of only 1 mμ, an effect which is commonly observed. A second set of samples was accordingly prepared by molding into shape. With both sets, experiments were made both on well annealed specimens, strain about 1 mμ, and on badly annealed specimens, strain about 50 mμ. The results are in Table XIII. 7.

TABLE XIII. 7—Effect of Strain on the Strength of Glass*

After Berndt

Glass	Strained		Annealed	
	Mean	Maximum	Mean	Maximum
Tensile Strength (Kilobars)				
Sawed	0.746	0.776	0.619	0.678
Molded	0.589	0.648	0.619	0.678
Crushing Strength (Kilobars)				
Sawed	14.92	18.06	13.92	16.60
Molded	15.12	16.00	17.77	20.53
Bending Strength (Kilobars)				
Sawed	0.677	0.756	0.845	0.864
Molded	1.109	1.255	1.060	1.100

* Composition near Table III. 4, No. 8.

Littleton and Preston[15] discussed the theory of thermally toughened glass, and showed that by producing a strongly compressed surface layer it is possible to increase the tensile strength of glass rods or bars by 50

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[35] Hovestadt-Everett, "Jena Glass," Macmillan, New York, 1902.

[36] Berndt, G., *Ber. deut. physik. Ges.*, 19, 314 (1917).

per cent, the bending strength by at least 150 per cent, with a theoretical limit of 230 per cent.

Meikle[37] compared the bending strength of a thermally toughened glass, known as "Armourplate," or "Securite," with untreated glass of the same composition. He used sheets 45 × 10 inches, supported on steel bars spread at 36-inch centers, and loaded midway between supports. The breaking strength, in pounds per square inch, for $\frac{1}{4}$-inch Armourplate, was 24,980; for $\frac{5}{16}$-inch, 27,160; and for untreated glass the corresponding values were 5,420 and 6,890.

Apelt[38] and Thierbach[39] studied the effect on the strength of deforming the rods under load below the annealing temperature, but were not able to establish a significant difference in the "mirror-free" strength,* although the area of mirror fracture was altered. Apelt also found that the chief difference between annealed and unannealed glass was in the amount of mirror fracture.

TABLE XIII. 8—Effect of Rate of Loading on the "Practical" and "Ultimate" Strength of Glass Rods *

After Apelt

Rate of loading (sec./kg.)	Area of rod, q	Practical strength Z	Ultimate strength Z_0	100 (s/q) and range	No. of tests
0.95 ± .1	1.31 ± .15	13.1 ± 1.3	14.1 ± 1.2	6.8 (3.4-10.0)	14
1.8 ± .1	1.37 ± .08	12.0 ± 1.0	12.9 ± 0.9	7.1 (5.2-10.9)	8
6.5 ± .02	1.34 ± .25	11.5 ± 2.3	13.3 ± 1.7	14.5 (5-33.6)	19
150 ± 36	1.39 ± .09	8.3 ± 0.4	11.4 ± 0.8	27.2 (19.9-34.9)	5
306 ± 42	1.32 ± .14	7.9 ± 1.4	12.6 ± 1.7	34.6 (10.9-58.9)	10
480 ± 72	1.40 ± .16	7.9 ± 1.0	11.3 ± 1.1	27.9 (13.2-74)	13
660 ± 72	1.45 ± .53	7.5 ± 1.5	12.9 ± 2.0	38.2 (19-63)	5
990 ± 240	1.48 ± .19	7.6 ± 0.9	11.9 ± 0.6	44.7 (29-68.4)	4

* Unit: kg./mm.^{2}

Effect of Duration of Loading on the Strength of Glass

The effect of long duration of load on the breaking strength was studied by Grenet,[40] using a plate glass from St. Gobain. The first experiments were made by loading in the middle strips, 3 × 25 mm. in section, with smoothed edges, supported at each end; the numbers given represent the mean of 20 observations agreeing to ± 15 per cent.

Duration of Load	Breaking Strength (Kilobar)
40 hours	0.33
2 hours	0.42
40 minutes	0.47
1 second	0.72

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* Cf. Müller, p. 323; Apelt, p. 324.

[37] Meikle, J., *J. Soc. Glass Tech.*, **17,** 149 (1933).

[38] Apelt, G., *Z. Physik*, **91,** 336 (1934).

[39] Thierbach, G., *Z. Physik*, **91,** 344 (1934).

[40] Grenet, L., *Bull. Soc. Encouragement*, **4,** 839 (1899). Cited by Le Chatelier, H., "La Silice et les Silicates," 309, Paris, 1914.

In a second series of experiments, in which the load was left on until the piece broke, the following results were obtained.

Load in kilobars	Broke after
0.3	2 days
0.25	3 months
0.20	Did not break in 4 months.

Preston[41] translated the original paper by Grenet, which contained interesting experimental detail. A "test plate" was placed on the specimen and illuminated by sodium light, thus giving a sensitive measure of deformation. "While the specimen was being loaded, the deflection of the glass produced a displacement of the fringes, and as soon as . . . the load became constant, the fringes ceased to move.

"When a load of six kilograms was reached, corresponding to a stress of four kilograms per square millimeter, no further load was added; thereupon the fringes ceased to move and at the end of two or three minutes fracture took place.

"While the last kilogram was added, 70 fringes were observed to pass (black band to black band, extinction to extinction); no displacement of the fringes was observed from the moment the writer ceased to add weight until the moment of fracture.

"As a movement of one-quarter of a fringe would certainly have been detected, it is seen that if there had been a permanent deformation (or creep) it must have been of the order of magnitude which corresponds to a very small increment of elastic deformation; in fact, the permanent set must have been less than the deflection caused by adding three and one-half grams weight."

Preston reports the following average breaking strengths for 20 specimens, in pounds per square inch. The plate glass used was of high quality, polished on the faces, diamond-cut on the edges, the diamond mark being on the compression face in a transverse test of the specimen, which was roughly one-fourth inch thick, two inches wide and 16 inches between supports. It had the percentage composition: SiO_2, 71.32; Na_2O, 13.00; CaO, 13.34; MgO, 0.23; Na_2SO_4, 0.95; NaCl, 0.73; As_2O_5, 0.17; $Fe_2O_3 + Al_2O_3$, 0.20.

Duration of test	5 sec.	1 min.	30 min.	4 hours
Average breaking strength	11,900	8,600	6,000	5,420

Similar results were obtained on a Foucault window-glass.

"The tests of long duration are particularly important, because it is far from clear whether the strength declines to some finite limit or

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[41] Grenet, L., *loc. cit.* Abridged translation by Preston, F. W., *Glass Ind.*, **15**, 277 (1934), supplemented in *J. Am. Ceram. Soc.*, **18**, 220 (1935).

whether it actually goes to zero on a very long test. . . . Several experimenters have suggested that the strength declines to about one-half; Littleton, in conversation, has suggested one-third; the present writer is inclined to think the ultimate strength may be zero."

Effect of Temperature on Strength

Little is known about the effect of temperature on the strength of glass. At ordinary temperatures Hooke's law appears to hold for glass up to fracture, and there is no region of plasticity. There is no evidence that with increased temperature a region of plasticity develops. As the temperature is increased, the diminution of viscosity makes the strength evanescent for loads of a duration decreasing with increasing temperature. This is illustrated by the results obtained by Laubengayer[42] on the collapsing temperatures of glass tubes of 13 mm. bore and 1.8 mm. wall-thickness, heated at 3° C. per minute, either open to the air or evacuated to 3 mm. pressure. The results are assembled in Table XIII. 9.

TABLE XIII. 9—Collapsing Temperatures of Glass Tubes

After Laubengayer

Glass	Temp. (° C)	
	Open	Evacuated
Soft soda-lime, Greiner and Fredericks	700	585
Resistance, Greiner and Fredericks	750	635
Pyrex, Corning Glass Works *	820	670
Bohemian Combustion	860	740
Moncrieff Combustion	820	770

* This probably refers to Pyrex chemical resistant glass, Table III. 3, No. 20.

Wartenberg[43] tested glass tubes under internal gas pressure at temperatures 40° to 50° below the "transformation point," and found that they withstood for the duration of the experiment (one hour) 80 per cent as much pressure as at 20°. He concluded that glass retains its strength undiminished up to the transformation point.

Brittleness

Brittleness is a term descriptive of the tendency of some substances to break or shatter when subjected to a stress exceeding the elastic limit, in contrast to the gradual and continuous deformation of a plastic substance under similar conditions. The term usually implies a shattering under sudden stress, and does not admit of precise definition or measurement.

Preston[44] listed the following requirements for a brittle substance:

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[42] Laubengayer, A. W., *Ind. Eng. Chem.*, **21**, 174 (1929); *Glass*, **6**, 111 (1929).

[43] Wartenberg, H. v., Greiner, B., Tabacznik, Z., Janeszewski, D., and Krawutschke, A., *Z. tech. Physik*, **13**, 479 (1932).

[44] Preston, F. W., *J. Am. Ceram. Soc.*, **15**, 176 (1932).

1. It must fail in tension and not in shear. This is equivalent to saying that the material breaks before it flows, and rules out ductile materials.
2. It should have a high value of the elastic modulus. This qualification is a matter of degree, and implies that the material fails at comparatively low strains. This rules out jellies.
3. It should have a fairly high tensile strength; otherwise the material is friable rather than brittle.
4. The material must be capable of developing forked fractures from internal stress. That is, a single fissure [45] must be capable of developing "radiants" of fissures, which are formed only when the fissure is travelling with explosive violence.

Brittleness usually is considered to be measured by the impact strength, or the energy required to destroy by impact, a formulation which is not consonant with the implications of brittleness. Föppl [20] defined brittleness as the ratio between compressive strength and impact strength, while Knapp [46] used the ratio of tensile strength to the product of the coefficient of expansion and Young's modulus. Most attempts to measure brittleness involve the measurement of the impact strength, or of the kinetic energy absorbed in breaking, but unanimity as to the calculation and dimensions of this quantity does not exist. Föppl subjected the glass to a series of blows the kinetic energy of which increased in geometrical progression, and used the total energy of the series of blows in his calculation. A similar procedure was followed by Gehlhoff and Thomas.[13] Graf,[47] Welter,[48] Williams,[21] and Guyer [49] used the energy of the final blow. Both Williams and Guyer used the formula ascribed to L. B. Tuckerman,

$$S = 18EW/Al,$$

in which the letters stand for the impact modulus in ft.-lb. per sq. inch, Young's modulus, the work in ft.-lb. expended to obtain a break, area and length, respectively. Preston [50] showed this formula to be dimensionally inhomogeneous and identical with the square of the maximum fiber stress. He used the square root of the above expression as the modulus of impact, thus obtaining a quantity directly comparable with the modulus of rupture, or tensile strength obtained in static tests. ". . . the maximum stress produced by the impact should be recorded. An impact produces vibrations, and the loop and node effects may result in stresses distinctly different from those calculated by the simple

[45] Preston, F. W., *J. Am. Ceram. Soc.*, **14,** 419 (1931).
[46] Knapp, O., *Glashütte*, **59,** 146 (1929).
[47] Graf, O., *Glastech. Ber.*, **3,** 153 (1925).
[48] Welter, G., *Z. Ver. deut. Ing.*, **70,** 773 (1926).
[49] Guyer, E. M., *J. Am. Ceram. Soc.*, **13,** 624 (1930).
[50] Preston, F. W., *J. Am. Ceram. Soc.*, **14,** 428 (1931).

assumptions of the Tuckerman formula, but if we decide to shrug our shoulders, and let it go at that, the logical thing to do is to take the square root of Tuckerman's S as representing the modulus of impact." It is probable that the "loop and node" effects mentioned by Preston may be the cause of the shattering effect implied in the concept of brittleness, which would afford justification for measuring brittleness by a formula involving a product of an elastic modulus and a strength modulus.

The impact is delivered either by a falling weight or by a loaded pendulum. Föppl used a 2 cm. cube placed on an anvil, and protected the upper surface with a steel plate. Repeated blows were delivered by dropping a weight from a series of heights increasing in geometrical progression until the piece broke. The total kinetic energy for n impacts is $n(n + 1)$ cm. kg. per cc. or kg. per cm. When the blow is delivered by a pendulum, the tup of the latter is usually of hardened steel, with the edges rounded off to form the segment of a sphere. Usually a succession of blows of increasing energy is delivered until the glass breaks; but Guyer measured the difference in the swing of the pendulum when free and when the swing was diminished in amplitude by the energy required to break the glass. Murgatroyd [51] discussed impact testing of glass, without giving any details of methods or of specifications.

The results of brittleness and impact tests are discordant and of doubtful significance. Several observers have found that results are dependent on the thickness of the specimen and strongly affected by the method. The results of Föppl are given in Table XIII. 10; the compositions of the glasses are given in Table III. 4. Graf broke the glass by a weight dropped on a horizontal piece of glass 20 cm. wide supported on wooden strips 25 cm. apart, and found that, using a 2.5 kg. weight, a fall of 18 cm. was necessary to break crystal glass 15 mm. thick, and a fall of 148 cm. for hard glass of the same thickness. His results were expressed in terms of $a = Gh/bs$ expressed in cm. kg. per

TABLE XIII. 10—Brittleness of Glass

After Föppl

Type and Table Ref.	Compressive Strength kg. per cm.^{2}	Impact Strength kg. per cm.^{2}	Brittleness Ratio
Borate Flint S389	6223	1046	4
Jena Geräteglas, III. 3, No. 4	8910	855	10
Flint O118, III. 4, No. 36	6273	430	15
Cylinder glass	9397	404	23
Normalglas, III. 4, No. 61	8770	259	34
Jena 59^{III}, III. 4, No. 56	9380	259	36
Heavy Flint S386	4470	98	46

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[51] Murgatroyd, J. B., *J. Soc. Glass Tech.*, **16**, 5 (1932).

sq. cm., in which G represents the weight dropped from a height h on a piece of glass of cross-section bs. Values of a ranged from about 0.3 to 2.0, but were highly discordant among themselves. Gehlhoff and Thomas attempted to ascertain the relation between impact strength and composition, using a pendulum method, but the results do not permit drawing conclusions. Preston[52] discussed the results of Guyer, and also privately communicated results by L. T. Sherwood, and concluded that when the correct formula was used the impact strengths obtained are slightly greater than the tensile strengths obtained under the usual static load, the ratios between impact strength and static strength averaging 1.42 in Guyer's results. Important factors frequently overlooked in measurements of brittleness are the short duration of the stress and the vibrations set up in the material.

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[52] Preston, F. W., *J. Am. Ceram. Soc.*, **14**, 432 (1931).

Chapter XIV

The Thermal Endurance of Glass

The ability to withstand thermal shock resulting from sudden difference in temperature is important in many uses of glass, and methods of measuring thermal endurance find application in the development of improved processes and in routine testing of glassware. Methods of testing thermal endurance are methods for breaking glass in tension by virtue of a differential thermal expansion, and failure in thermal endurance tests is determined by the same factors which determine failure in other types of strength measurements, namely, the influence of those disturbing factors which are grouped under the term "flaws." In all cases the tests have been applied to specific shapes or articles, and the conclusions refer, not to the properties of glass as such, but to the glass articles tested.

Several formulas have been developed for the calculation of thermal endurance from those properties of the glass which affect (1) the development and distribution of strain and (2) failure under stress: these properties include thermal expansion, Young's modulus, Poisson's ratio, thermal conductivity and diffusivity, and tensile strength. Tests made to confirm these formulas have not given good agreement with theory; but in general all the properties included in the calculation have not been measured but have been calculated from the composition by the use of factors. The influence of shape has not been adequately considered; assumptions have been made as to cooling rates; the values used for tensile strength, which have been deduced from different types of measurements, have even less meaning than in their usual application; and the testing methods have been open to criticism. "It is doubtful if the use of any of these formulas in comparing various glasses offers any advantage over the comparison of expansion coefficients alone. The coefficient of expansion is more affected by difference in composition than are Young's modulus, Poisson's ratio, or the tensile strength. Moreover, since the tensile strength is largely determined by surface conditions, the breakage of glasses of similar expansion properties under thermal shock will be determined largely by the condition of their surfaces. This fact is the explanation of the greater thermal resistance of "toughened" glass and also of the erratic results usually obtained in carrying out tests of this property."[1] A similar conclusion was reached by Schönborn.[2]

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[1] Littleton, J. T., and Morey, G. W., "The Electrical Properties of Glass," Wiley, New York, 1933.

[2] Schönborn, H., *J. Soc. Glass Tech.*, 20, 475 (1936).

Winkelmann and Schott[3] made a study of thermal endurance, using cubes of glass one and two cm. on a side, which were dropped into cold water after having been heated to successively increasing temperatures. Their theoretical discussion assumed a very thick plate of glass, bounded by an infinitely extended plane face, originally of uniform temperature θ_1. This face was assumed to be suddenly lowered to the temperature θ_0, and maintained at that temperature. An analysis of the problem led to the definition of a coefficient of thermal endurance, *F*, defined by the expression,

$$F = \frac{P}{\alpha E}\sqrt{\frac{K}{sl}} = B(\theta_1 - \theta_0),$$

in which *P* is the tensile strength, α is the linear coefficient of thermal expansion, *E* is Young's modulus, *K* is thermal conductivity, *s* is density, *c* is specific heat, and *B* is a constant. Comparison was made between the order in which the 20 glasses tested were arranged by experiment and by calculation of *F*, in which calculation several of the quantities involved were themselves calculated by means of empirical factors. Several later observers have recalculated the results of Winkelmann and Schott, frequently giving them more weight than they deserve. The two arrangements agreed for the most part, with some exceptions. Winkelmann and Schott also showed that glass could withstand much greater temperature differences when suddenly heated than when suddenly cooled, and confirmed their conclusions by experiment. A sample of glass which had shown an abnormally low thermal endurance when chilled, a 2-cm. cube having broken from a temperature difference of 52.8°, did not crack when plunged into molten tin, a temperature difference of 465°.

Everett[4] discussed the case of a sphere, of temperature θ_1, with its surface so rapidly cooled to θ_0 that only a relatively thin layer had changed its temperature at the time cracking occurred. He obtained for the maximum difference of temperature the sphere could withstand

$$\theta_1 - \theta_0 = (1 - \sigma)\frac{P}{\alpha E},$$

in which σ represents Poisson's ratio. When the glasses studied by Winkelmann and Schott were rearranged in the order given by this expression, the agreement with experiment was only a little better.

Stott[5] considered a specimen free from strain, at a uniform temperature, and imagined the surface divided into three sections. The first section is in contact with a body impervious to heat, the second is main-

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[3] Winkelmann, A., and Schott, O., *Ann. Physik Chem.*, **51**, 730 (1894)

[4] Hovestadt-Everett, "Jena Glass," Macmillan, New York, 1902.

[5] Stott, V. H., *J. Soc. Glass Tech.*, **8**, 139 (1924).

tained at θ_0, the third has its temperature suddenly changed to θ and maintained at that temperature. The glass is assumed to break after a time, t, at a temperature difference, θ_c, and the deformation just before breaking is ζ. Thermal diffusivity, D, $= k/sc$, in which k is thermal conductivity, s is density, and c is specific heat. From dimensional analysis he obtained the expressions

$$(\theta - \theta_0) = \left(\frac{1}{\alpha}\right) \varphi \left[\zeta, \sigma, \left(\frac{1}{l}\right) \sqrt{kt/sc} \right. \tag{1}$$

$$(\theta_c - \theta_0) = \left(\frac{1}{\alpha}\right) F(\zeta, \sigma) \tag{2}$$

Equation (1) determines the time which elapses before rupture takes place, after a given change in temperature; equation (2) determines whether or not a given change in temperature causes rupture. Thermal conductivity does not enter into (2), in contrast to the corresponding expression deduced by Winkelmann and Schott. Their treatment assumed that the time required to break the specimen was the same for every glass, which could be true only if the time were zero. Further complications arise from the usual assumption that the temperature of a part of the surface is brought instantaneously from θ_0 to θ_c. Equation (2) indicates that thermal endurance is proportional to the reciprocal of thermal expansion and to a function of ζ and σ; assuming that function to be proportional to $(PE/(1 - \sigma)$ gives the expression

$$(\theta_c - \theta_0) = \frac{P(1 - \sigma)}{\alpha E},$$

in agreement with Everett.

Stott, who tested the above formula by the data of Winkelmann and Schott, obtained slightly better agreement than that in the original publication. Values of many of the properties which enter into the calculation were obtained by means of Winkelmann and Schott's factors for those properties, and the uncertainties thus introduced greatly diminished the value of the calculation. Stott and Irvine[6] tested cubes of glass, but they dropped the specimens into water, instead of removing them from the furnace and plunging them into water by hand, as had been done by Winkelmann and Schott. Probably because of the more rapid immersion, Stott and Irvine found that larger temperature differences were necessary to cause fracture, in the ratio of about 250° to 148°. A variable present in the earlier work accordingly was the speed of immersion of the samples, which probably was different in manual repetitions of the chilling operations, and it may have been as important a factor as the properties of the glass.

[6] **Stott, V. H., and Irvine, E., *J. Soc. Glass Tech.*, 8, 148 (1924).**

H. V. Mallison, in a paper by Gould and Hampton,[7] discussed the cooling of glass in more general terms, with special reference to the chilling of beakers filled with hot paraffin. The expression obtained was

$$\theta_0 = \frac{P(1-\sigma)}{\alpha E} \cdot \frac{1}{F(X,T)},$$

in which θ_0 is the temperature difference necessary to cause fracture. The function of X and T is a complicated factor, involving the size and shape of the test-piece, the thermal diffusivity of the glass, and a constant, c, dependent on the liquid used. Application of the equation required assuming a value of the constant c; and the value assumed was such as to make the surface temperature fall to 10 per cent of its initial value in 0.02 second. With a thickness of 1 mm., the maximum value of the surface stress was reached in 0.04 second, and was 1.71 times the value when conditions were steady. When the thickness of the plate had the values 0.5, 1.0, and 2 mm., the relative maxima of stress were in the ratios 0.743, 0.855, 0.917, respectively; and the relative maximal values of stress ranged from unity for a very thick slab to zero for an infinitely thin one.

"From the theoretical expression, it follows that the temperature of fracture of an infinitely thick plate (in actual figures, this is roughly anything thicker than 1 cm.) should be given by the expression (Everett's equation) $P(1 - \sigma)/\alpha E$, and that for an infinitely thin plate the temperature of fracture should be just double this value. All the experimental evidence, however, is against this. The range of temperature values is certainly more than two to one."[8] Hampton then modified the theory by using the formula proposed by Gooding for the tensile strength of rods, $P = A(B/d)$, in which A and B are constants, and d is the diameter of the rod. Assuming $c = 5$, he obtained relative breaking temperatures corresponding to various thicknesses, as follows: ∞, 1.00; 0.60 cm., 1.19; 0.50 cm., 1.23; 0.40, 1.28; 0.30, 1.40; 0.20, 1.62; 0.15, 1.87; 0.10, 2.37; 0.05, 3.24; 0.025, 4.68.

Gould and Hampton studied thermal endurance by plunging beakers filled with hot paraffin into cold water, and by increasing the temperature difference by steps of 5° until the sample broke. They found a relation between the maximum thickness of beaker $= 2\,b$ and the temperature drop θ of

$$\theta\sqrt{2b} = \text{const} = B$$

and this relation was used for correcting beakers to standard thickness of 1 mm., within the interval 0.9 to 1.9 cm. Warren[9] expressed the above relation as: $B = \theta l^n$, in which l is the thickness. Gould and

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[7] Gould, C. E., and Hampton, W. M., *J. Soc. Glass Tech.*, **14**, 188 (1930).

[8] Hampton, W. M., *J. Soc. Glass Tech.*, **20**, 461 (1936).

[9] Warren, W. J. A., *J. Soc. Glass Tech.*, **14**, 313 (1930).

Hampton found n to be 0.5; Warren found it to change with thickness, ranging from 0.36 to 0.4 for beakers of average thickness of 1.4 mm., and reaching 0.5 at a thickness of 1.1 mm. He preferred the linear equation

$$B = \theta + (l - 1)\,A,$$

where A is an empirical constant, found from experiment to be $A = \frac{B}{3.75}$.

Warren found that slight modifications in procedure, such as shielding from draught, did not influence the results. It was necessary that the position of maximum thickness be within the concave portion of the bottom of the beaker, but otherwise the effect of uneven distributions of glass was unimportant. He found the thermal endurance of beakers of composition of sheet glass to decrease with time, even after several months, a result which requires confirmation.

Gould and Hampton compared the observed values of thermal endurance with those calculated from the formula previously given, assuming a value of 0.25 for Poisson's ratio. The value of $F(X, T)$ should be between 1 and 1.2 for the beakers used. Values of P and E were calculated from the factors proposed by Winkelmann and Schott, and a "slightly modified series of English and Turner's factors" was used for the calculation of α. The ratios of the calculated and the observed values ranged from 1.09 to 1.48, although 8 of the 11 glasses gave a ratio of 1.18 or less, with an average of 1.14.

Knapp[10] took exception to the factors used by Gould and Hampton, and to the use of 0.25 for Poisson's ratio. He considered the formula used to be inapplicable to beakers, and advocated the formula

$$T = 404\,(\log W - 07),$$

in which W is the thermal endurance calculated from the factors given by Winkelmann and Schott.

The Glass Standards Committee of the Society of Glass Technology adopted as a provisional standard test of thermal endurance[11] the chilling of a beaker filled with melted paraffin wax by plunging into water at 15° C. The standard beaker is of conical form, nominal capacity 200 cc., with dimensions specified, thickness 1 mm. Beakers should be tested not less than two hours, or more than 48 hours, after manufacture, and should be of a satisfactory standard of annealing. Enough paraffin is used to give a depth of liquid of 4 or 5 cm. Testing should be commenced at a temperature 50° below that at which breakage is expected, and the tests repeated at 5° intervals until the beakers are broken. The process is repeated on several beakers, and those which are less than

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[10] Knapp, O., *Keram. Rundschau*, **39**, 459 (1931); *Abs. J. Soc. Glass Tech.*, **15**, 477 (1931).

[11] *J. Soc. Glass Tech., Proc.*, **14**, 160 (1930).

0.9 mm., or greater than 1.9 mm. thick are rejected. From the average results for ten satisfactory beakers, thermal endurance is calculated from the formula:

Thermal endurance = temperature difference × thickness in mm.

The earlier work on thermal endurance was done with cubes; much of the later work with beakers; and recently rods have been advocated for this test. They are convenient shapes, and may be readily plunged into water from a hot furnace under standard conditions. Hampton[8] stated that in many instances spiral cracks form which are practically invisible, and that the rod will withstand several heatings before complete fracture occurs. This introduces an element of uncertainty, which, however, has not been noticed by other observers. Gould and Hampton[7] found the relation between the constant B, in the formula connecting the thickness of a beaker and the temperature drop necessary to cause fracture, and the corresponding constant R, for the temperature drop required to break rods 3 to 5 mm. in diameter, to be $R = 1.33\,B$.

Seddon,[12] in a report of the Glass Standards Committee of the Society of Glass Technology, discussed at some length a test carried on jointly by several English glass manufacturers on the use of rods in tests of thermal endurance. The rods, 2.54 cm. (1 inch) long and of several diameters, were prepared from the same gathering of glass, and the ends were rounded in the fire just sufficiently to remove only the sharp edge. The rods were heated in a horizontal-tube electric furnace having a constant temperature zone 2 to 3 in. long. The furnace was heated to 100° with five rods in position; the rods were given time to reach the temperature of the furnace, then taken out, one at a time by means of a rake, the handle of which projected from the furnace, and dropped into water at 20°. The unbroken specimens were dried and reheated to a higher temperature, and the operation repeated, with 5° increments of temperature, until all were cracked.

The results from the several laboratories on rods 3 to 4, 4 to 5, and 5 to 6 mm. in diameter were studied statistically,[13] from which study the following conclusions were drawn. Rounding the edges of the rods appeared to increase the consistency of the results. The temperature shock required to cause fracture definitely increased with diameter; an increase in diameter of 1 mm. lowered the temperature difference required to cause fracture by an amount lying between 10.4° and 12.4° for a commercial "lime-soda" glass. The thermal endurance test appeared to give good results for normal glasses, but with heat-resisting glasses difficulties appeared, and the discrepancies between the results of different

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[12] Seddon, E., *J. Soc. Glass Tech.*, **20**, 498 (1936).

[13] See also, Dudding, B. P., and Baker, I. M., *J. Soc. Glass Tech.*, **17**, 239 (1933).

observers, real with normal glasses, were increased when the temperature drop required to cause fracture exceeded 250°.

Schönborn[14] also studied the thermal endurance of glass rods, and distinguished between "technical thermal endurance," the difference in temperature at which the first cracks (these are generally longitudinal and are caused by some flaw) appear, and "true thermal endurance," the temperature difference at which the first transverse cracks appear. Rounding the ends of the rods had little effect on true thermal endurance, but it increased the technical thermal endurance and decreased the scattering of the results. Unannealed rods gave a higher thermal endurance. Thin rods, up to 5 mm. in diameter, cracked partially at the moment of immersion, but thicker rods, over 1 cm., gave intervals sometimes as long as three or four seconds. This delayed cracking may be explained by a decrease in strength with time.

Murgatroyd[15] suggested testing for thermal endurance of hollow ware by filling the cold vessels with hot liquid, and claimed the test was accurate in performance and required a smaller number of pieces. It is suitable for bottles only. Douglas[16] discussed the testing of illuminating ware. Thermal endurance tests on specimens of simple form may give misleading results with ware the shape of which is guided by artistic or technical design, in which, even if thoroughly annealed, thermal stresses have been set up by the method of use. For such shapes a test in which drops of water fall on the piece under service conditions is useful. There is a decrease in thermal endurance as the size of the drop is increased above a minimum, followed by an increase to a maximum with drops a little less than 0.1 g. in weight, followed by a further decrease.

Douglas further discussed the lack of correlation between the behavior of glass tubing when heated before the blowpipe, and tests of thermal endurance made by dropping a heated specimen into water. A better correlation with practice was found with a test in which cold mercury was forced into the heated tube, which more closely resembled the stress conditions in use.

Tabata and Moriya[17] derived the equation

$$\theta_c = \frac{P(1-\sigma)}{\alpha E} \cdot \frac{1}{F(h \cdot R)},$$

in which R is the radius, and h is dependent on the cooling agent. For the relation between the radius of the glass rod and the temperature drop, θ_c, they deduced the equation

$$\theta_c \; (R^m - nR) = c,$$

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[14] Schönborn, H., *J. Soc. Glass Tech.*, **20**, 475 (1936).
[15] Murgatroyd, J. B., *J. Soc. Glass Tech.*, **20**, 511 (1936).
[16] Douglas, R. W., *J. Soc. Glass Tech.*, **20**, 517 (1936).
[17] Tabata, K., and Moriya, T., *J. Am. Ceram. Soc.*, **17**, 34 (1934).

the constants of which were found by experiment to be: $m = 0.636$, $n = 0.528$, $c = 53.0$. The experiments were made on annealed rods ranging from 0.32 to 0.62 cm. in diameter, 3 cm. long, with fire-rounded ends. In a later paper[18] they gave the results on a series of 30 glasses, of the general formula $x\,K_2O$, $(1 - x)\,Na_2O$, $z\,B_2O_3$, $y\,SiO_2$, in which x, y, and z denote the number of molecules of the given components. The samples were approximately 5 mm. in diameter, 3 cm. long, annealed, with fire-polished ends, heated on a support in a vertical electric furnace, and dropped into water below. The relation between thermal endurance and chemical composition was of approximately parabolic form.

TEMPERATURE DISTRIBUTION AND STRESSES: OPTICAL PATH DIFFERENCES DUE TO THERMAL GRADIENTS *

Temperature Distribution During Heating and Cooling

The first step in the estimation of the thermal stresses produced in glass is the calculation of the temperature gradients under the assumed conditions.

For the case of the sudden change of surface-temperature the three most generally useful † formulas are:

Slab

$$H = 2\sum_{m=1}^{m=\infty}\left\{\frac{1}{Q_m(-1)^{m+1}}\,e^{\frac{-\kappa Q^2{}_m t}{a^2}}\cos\left(\frac{Q_m x}{a}\right)\right\} \tag{1}$$

Cylindrical rod

$$H = 2\sum_{m=1}^{m=\infty}\left\{\frac{1}{R_m J_1(R_m)}\,c^{\frac{-\kappa R^2{}_m t}{a^2}}J_0\left(\frac{R_m x}{a}\right)\right\} \tag{2}$$

Sphere

$$H = 2\sum_{m=1}^{m=\infty}\left\{\frac{1}{S_m(-1)^{m+1}}\,e^{\frac{-\kappa S^2{}_m t}{a^2}}\frac{a}{x}\sin\left(\frac{S_m x}{a}\right)\right\} \tag{3}$$

where

$$H = \frac{\theta - \theta_f}{\theta_i - \theta_f}$$

θ is the temperature at any point; θ_i, the initial uniform temperature of the solid; θ_f, the constant temperature of the surface; κ, the thermal

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[18] Tabata, K., and Moriya, T., *J. Soc. Glass Tech.*, **20**, 524 (1936).

* This section is reprinted, with minor alterations, from Adams, L. H., and Williamson, E. D., *J. Franklin Inst.*, **190**, 597, 835 (1920).

† For points close to the surface or for small values of t the infinite series (1), (2), and (3) are not very rapidly convergent. Under these conditions the following formulas are more convenient:

diffusivity (equal to the thermal conductivity divided by the product of the specific heat and the density); t, the time; a, one-half the diameter or thickness; x, the distance from the centre; J_0 ( ) and J_1 ( ) are Bessel's functions of the zeroth and first order; m is any integer; and Q_m, S_m, and R_m are written respectively for $(2_m - 1)\pi/2$, $m\pi$, and the roots of the equation $J_0(x) - 0$.

For the case of linear heating of the surface, we have the corresponding equations:

Slab

$$\theta = ht - \frac{h}{2\kappa}(a^2 - x^2) + \frac{2ha^2}{\kappa}\sum_{m=1}^{m=\infty}\frac{1}{Q_m^3(-1)^{m+1}}e^{\frac{-\kappa Q_m^2 t}{a^2}}\cos Q_m\left(\frac{x}{a}\right). \tag{4}$$

Cylinder

$$\theta = ht - \frac{h}{4\kappa}(a^2 - x^2) + \frac{2ha^2}{\kappa}\sum_{m=1}^{m=\infty}\frac{1}{R_m^3 J_1(R_m)}e^{\frac{-\kappa R_m^2 t}{a^2}}J_0\left(R_m\frac{x}{a}\right). \tag{5}$$

Sphere

$$\theta = ht - \frac{h}{6\kappa}(a^2 - x^2) + \frac{2ha^2}{\kappa}\sum_{m=1}^{m=\infty}\frac{1}{S_m^3(-1)^{m+1}}e^{\frac{-\kappa S_m^2 t}{a^2}}\frac{a}{x}\sin\left(S_m\frac{x}{a}\right). \tag{6}$$

When t becomes large with respect to a, the last term of (4), (5), or (6) vanishes, and the temperature gradient reaches a "steady state," in which the temperature distribution is represented by a parabola. The equations for this steady state are:

Slab

$$\theta = ht - \frac{h}{2\kappa}(a^2 - x^2) \tag{7}$$

Sphere

$$1 - H = \frac{2a}{x\sqrt{\pi}}\left\{\int_{q_0-q}^{q_0+q}e^{-z^2}dz + \int_{3q_0-q}^{3q_0+q}e^{-z^2}dz + \int_{5q_0-q}^{5q_0+q}e^{-z^2}dz + \ldots\ldots\right\}$$

Slab

$$1 - H = \frac{2}{\sqrt{\pi}}\left\{\int_{q_0-q}^{3q_0+q}e^{-z^2}dz + \int_{q_0+q}^{3q_0-q}e^{-z^2}dz + \int_{5q_0-q}^{7q_0+q}e^{-z^2}dz + \int_{5q_0+q}^{7q_0-q}e^{-z^2}dz + \ldots\ldots\right\}$$

or

$$H = \frac{2}{\sqrt{\pi}}\left\{\int_{0}^{q_0-q}e^{-z^2}dz - \int_{q_0+q}^{3q_0-q}e^{-z^2}dz + \int_{3q_0+q}^{5q_0-q}e^{-z^2}dz - \ldots\ldots\right\}$$

where z is an integration variable, $q = x/2\sqrt{\kappa t}$, $q_0 = a/2\sqrt{\kappa t}$ and H, a, x, K and t have the same meaning as above. *Cf.* Woodward, R. S., *Phys. Rev.* 16, 176, 177 (1903); and Queneau, A. L., *School of Mines Quart. of Columbia Univ.*, 23, 181-195 (1902).

Cylinder

$$\theta = ht - \frac{h}{4\kappa}(a^2 - x^2) \tag{8}$$

Sphere

$$\theta = ht - \frac{h}{6\kappa}(a^2 - x^2) \tag{9}$$

Finally for linear heating of cylindrical tubes and spherical shells, if a_1 and a_2 are respectively the internal and external radii, we have the steady state equations.*

Cylindrical tube.—(*a*) Heat transfer taking place only at outside,

$$\theta = ht - \frac{h}{4\kappa}\left(a_2^2 - x^2\right) + \frac{ha_1^2}{2\kappa}\ln\frac{a_2}{x} \tag{10a}$$

(*b*) Heat transfer taking place equally at inside and outside,

$$\theta = ht + \frac{hx^2}{4\kappa} + \frac{h\left(a_1^2 \log\dfrac{x}{a_2} - a_2^2 \log\dfrac{x}{a_1}\right)}{4\kappa \log\dfrac{a_2}{a_1}} \tag{10b}$$

Spherical shell.—Heat transfer taking place only at outside,

$$\theta = ht + \frac{h(x^2 - a_2^2)}{6\kappa} + \frac{ha_1^3}{3\kappa}\left(\frac{1}{x} - \frac{1}{a_2}\right) \tag{11}$$

Stresses due to temperature gradients.—These stresses may be evaluated from the following equations: in which α is the coefficient of linear (thermal) expansion, $e = \dfrac{1}{3R} + \dfrac{1}{9K}$, $f = \dfrac{1}{6R} - \dfrac{1}{9K}$ and θ' is the difference between the temperature at any point and the temperature of the surface.

Slab

$$F = \frac{C_1 - \alpha\theta'}{e - f} \tag{12}$$

where

$$C_1 = \frac{\alpha}{a}\int_0^a \theta' dx \tag{12a}$$

and F is the tension in any direction parallel to the faces of the slab.

Cylindrical Tube.—If the temperature distribution be symmetrical

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* The general equations corresponding to (10a), (10b), and (11) can be obtained by the proper substitutions.

about the axis, F_a, F_r, and F_t, the axial, radial, and tangential stresses may be obtained from the three equations:

$$(e-f)F_a + \alpha\,\theta' = C_1 \tag{13a}$$

$$xF_r{}^2 = -\frac{\alpha}{e-f}\int x\theta'\mathrm{d}x + \frac{C_2x^2}{2} + C_3 \tag{13b}$$

$$F_t = F_r + x\frac{\mathrm{d}P_r}{\mathrm{d}x} \tag{13c}$$

C_1, C_2, and C_3 being constants of integration which are evaluated from the boundary conditions. For a solid cylinder the same equations apply, except that C_3 is zero.

*Spherical shell.**—With temperature distribution symmetrical about the centre, we have

$$x^3F_r = -\frac{2\alpha}{e-f}\int x^2\theta'\mathrm{d}x + C_1\frac{x^3}{3} + C_2 \tag{14a}$$

$$F_t = F_r + \frac{x}{2}\frac{\mathrm{d}F_r}{\mathrm{d}x} \tag{14b}$$

C_1 and C_2 being integration constants. For a solid sphere C_2 vanishes.

The above equations may be used to determine the stresses in the various solids when the heating or cooling is carried out in a certain specified manner. As an example of their application, we may consider (A) linear heating of the surface, and (B) sudden change of surface temperature.

(A) *Surface Heated at Constant Rate.* (*Steady State.*)

(*1*) *Slab.*—From equations (7), together with (12) and (12a)

$$F = \frac{\alpha h}{6\kappa(e-f)}(a^2 - 3x^2) \tag{15}$$

(*2a*) *Cylindrical tube, heated on outside only.*—From equations (10), together with (13a), (13b), and (13c)

$$F_a = \frac{\alpha h(a_2{}^2 - x^2)}{4\kappa\,(e-f)} + \frac{\alpha h a_1{}^2}{4\kappa\,(e-f)}\left(\ln\frac{x^2}{a^2{}_2} - 1\right) \tag{16}$$

$$F_r = -\frac{\alpha h x^2}{16\kappa\,(e-f)} + \frac{\alpha h a_1{}^2}{4\kappa\,(e-f)}(\ln x - \tfrac{1}{2}) + \frac{C_1}{2} + \frac{C_2}{x^2} \tag{16b}$$

$$F_t = -\frac{3\alpha h x^2}{16\kappa\,(e-f)} + \frac{\alpha h a_1{}^2}{4\kappa\,(e-f)}(\ln x + \tfrac{1}{2}) + \frac{C_1}{2} - \frac{C_2}{x_2} \tag{16c}$$

C_1 and C_2 can be immediately evaluated by placing $F_r = 0$ for $x = a_1$ and $x = a_2$.

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* While the equations for the sphere are exact, those for the slab and cylinder involve the assumption that end-effects can be neglected, but when the thickness or diameter is small in comparison with the other dimensions, the error introduced by this assumption is probably very small.

(*2b*) *Limiting case for small bored tube* (*a_1 negligible compared to a_2*).

$$F_a = \frac{\alpha h(a_2^2 - 2x^2)}{8\kappa\,(e-f)} \tag{17a}$$

$$F_r = \frac{\alpha h\left(a_2^2 - x^2 - \dfrac{a_2^2 a_1^2}{x^2}\right)}{16\kappa\,(e-f)} \tag{17b}$$

$$F_t = \frac{\alpha h\left(a_2^2 - 3x^2 + \dfrac{a_2^2 a_1^2}{x^2}\right)}{16\kappa\,(e-f)} \tag{17c}$$

(*2c*) *Solid cylinder.*—From equations (8), together with (13a), (13b), and (13c), C_3 being zero,

$$F_a = \frac{\alpha h(a^2 - 2x^2)}{8\kappa\,(e-f)} \tag{18a}$$

$$F_r = \frac{\alpha h(a^2 - x^2)}{16\kappa\,(e-f)} \tag{18b}$$

$$F_t = \frac{\alpha h(a^2 - 3x^2)}{16\kappa\,(e-f)} \tag{18c}$$

(*3a*) *Spherical shell, heated on outside surface only.*—From equation (11), together with (14a) and (14b), putting $F_r = 0$ at $x = a_1$, and $x = a_2$,

$$F_r = \frac{\alpha h}{15\kappa\,(e-f)}\left\{-x^2 - \frac{5a_1^3}{x} + \frac{a_2^5 + 5a_2^2 a_1^3 - 6a_1^5}{a_2^3 - a_1^3} - \frac{a_2^5 a_1^3 - 6a_2^3 a_1^5 + 5a_2^2 a_1^6}{(a_2^3 - a_1^3)x^3}\right\} \tag{19a}$$

$$F_t = \frac{\alpha h}{15\kappa\,(e-f)}\left\{-2x^2 - \frac{5a_1^3}{2x} + \frac{a_2^5 + 5a_2^2 a_1^3 - 6a_1^5}{a_2^3 - a_1^3} - \frac{a_2^5 a_1^3 - 6a_2^3 a_1^5 + 5a_2^2 a_1^6}{2(a_2^3 - a_1^3)x^3}\right\} \tag{19b}$$

(*3b*) *Limiting case for very small internal diameter* (*a_1 negligible compared to a_2*).

$$F_r = \frac{\alpha h}{15\kappa\,(e\text{-}f)}\left(-x^2 + a_2^2 - \frac{a_2^2 a_1^3}{x^3}\right) \tag{20a}$$

$$F_t = \frac{\alpha h}{15\kappa\,(e\text{-}f)}\left(-2x^2 + a_2^2 + \frac{a_2^2 a_1^3}{2x^3}\right) \tag{20b}$$

(*3c*) *Solid sphere.*—From equation (9), together with (14a) and (14b), C_2 being zero,

$$F_r = \frac{\alpha h}{15\kappa\,(e\text{-}f)}(a^2 - x^2) \tag{21a}$$

$$F_t = \frac{\alpha h}{15\kappa\,(e\text{-}f)}(a^2 - 2x^2) \tag{21b}$$

Approximate equations for glass (linear heating).—For most glasses α is about 7.9×10^{-6} per deg. C., κ is about 0.004 cm.^{2}/sec., or 0.24 cm.^{2}/min., and from the values of K and R, $e - f\left(= \dfrac{1}{6R} + \dfrac{2}{9K}\right)$

is about 1.2×10^{-6} cm.²/kg. Hence, if F is measured in kg/cm.² and h deg./min. (being positive for heating), we have the following approximate equations (tension being reckoned as positive and compression as negative).

Slab

$$F = 4.6h(a^2 - 3x^2) \qquad (22)$$

At the middle, $x = 0$, and therefore

$$F = 4.6ha^2 \qquad (22a)$$

while at the surface, $(x = a)$

$$F = -9.2ha^2 \qquad (22b)$$

Solid cylinder

$$F_a = 3.4h(a^2 - 2x^2) \qquad (23a)$$
$$F_r = 1.7h(a^2 - x^2) \qquad (23b)$$
$$F_t = 1.7h(a^2 - 3x^2) \qquad (23c)$$

Solid sphere

$$F_r = 1.8h\ (a^2 - x^2) \qquad (24a)$$
$$F_t = 1.8h(a^2 - 2x^2) \qquad (24b)$$

(B) *Sudden Change of Surface Temperature.*

In this case the application of the proper temperature distribution equations to the general stress equations yields, as already shown for the case of linear heating, the desired equation for the sudden change of surface temperature. Only one such equation will be given here, namely, that for the infinite slab. The combination of equations (1) and (12) leads to the relation:

Slab

$$F = \frac{2\alpha(\theta_i - \theta_f)}{C}\sum e^{\frac{-\kappa Q_m^2 t}{a^2}}\left\{\frac{1}{Q_m^2} - \frac{(-1)^{m+1}}{Q_m}\cos\frac{Q_m x}{a}\right\} \qquad (25)$$

in which $C = \dfrac{1}{6R} + \dfrac{2}{9K}$, K being the modulus of compressibility, R the modulus of rigidity. The remaining symbols have the meanings already explained.

In Fig. XIV. 1 the distribution of a stress in a slab 2 cm. thick, initially at 100° and suddenly plunged into a bath at 0°, is shown for several elapsed times. The stress distribution was calculated from equation (25) and the numerical values of a, κ, K and R were taken as the approximate average for various kinds of glass.

Optical Path Differences

From the stress equations already given, the optical path differences as observed between crossed nicols may be readily calculated.

Some examples will be given for the case of temporary stresses due to linear heating. These formulas also give a close approximation to the distribution of birefringence in strained glass objects such as are ordinarily encountered.

Slab.—When a slab or plate is viewed lengthwise, the longitudinal stresses in the line of sight produce no birefringence and (except near the edges) there are no transverse stresses. Hence the observed path difference at any point is due only to the single set of longitudinal stresses normal to the line of sight, that is, parallel to the faces of the plate and perpendicular to direction of the beam of light. The stress is given by equation (22) and the birefringence is B times the stress at any point. Hence,

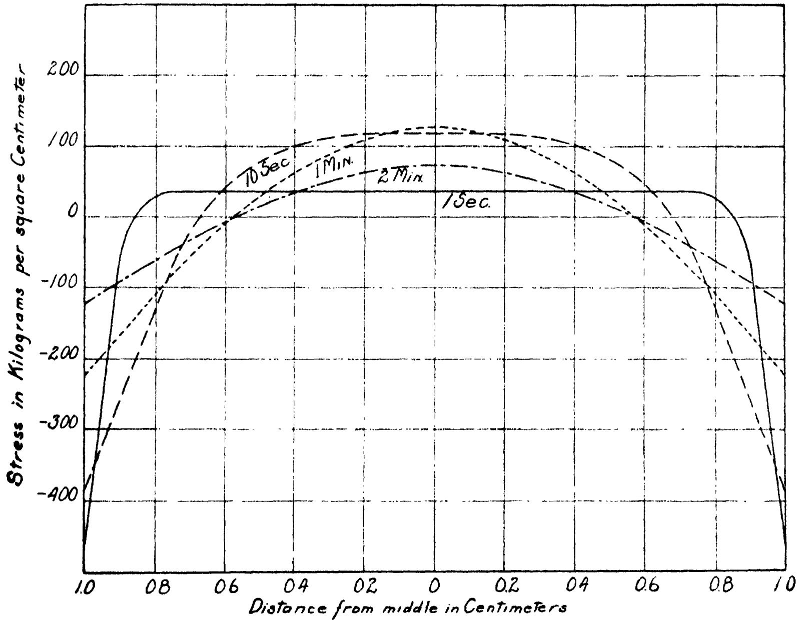

FIGURE XIV. 1.—Curves showing the distribution of stresses in a plate of glass two centimeters thick, which, initially at zero degrees C., is suddenly plunged into a bath at 100° C. The full line indicates the stresses throughout the glass after one second has elapsed; the broken line, after ten seconds; the dotted line, after one minute; the dot-dash line, after two minutes. After Adams and Williamson.

$$\Delta n = 4.6\, Bh\, (a^2 - 2x^2) \tag{26}$$

and along the middle,

$$\Delta n = 4.6\, Bha^2 \tag{27}$$

Since B is ordinarily about 2.8 for ordinary glass (when Δn is expressed in mμ per cm.), we may write

$$\Delta n = 13\, ha^2 \tag{28a}$$

and for the optical path difference, δ, (along the middle), we have obviously

$$\delta = 13\, ha^2 l \tag{28b}$$

where l is the length of the block in the line of sight.

In order to verify these equations experimentally, a slab of ordinary crown glass 7.6 cm. long and 2.2 cm. thick was heated at a constant rate of 3.8 deg. per min. The optical path difference along the middle was found to be 402mμ. The birefringence was therefore $\frac{402 \times 10^{-7}}{7.6} = 52.9 \times 10^{-7}$, or 52.9m$\mu$ per cm. The value of B for ordinary crown glass is 2.57. Hence, by equation (28a) the birefringence should have been $4.6 \times 2.57 \times 3.8 \times \left(\frac{2.2}{2}\right)^2 = 54.3m\mu$ per cm. Another experiment with a different heating rate gave 60.2 and 60.9 for the birefringence calculated, respectively, from the heating rate and from the observed path difference.

Cylinder.—When a cylinder is viewed along its axis, the calculation of the birefringence distribution is simple. In this case the axial stresses produce no effect, and the path difference is due to difference of the radial and tangential stresses. Hence, from equations (23b) and (23c)

$$\Delta n = 3.4\, B\, h\, x^2 \tag{29}$$

The sign of the birefringence is such that for a cylinder which is being heated or for a cylinder which is permanently strained, γ (the greater index) is in the radial direction.

The following observation is an example of the use of equation (29): A section of a cylindrical glass rod 2.0 cm. in diameter, when viewed lengthwise, showed at the surface a birefringence equal to 2.1×10^{-4} (2100mμ per cm.). The rod was of soda lime glass of unknown composition, but it is safe to assume that the value of B is not far from 2.8. Hence, by equation (29) the value of h is $\frac{2100}{2.8 \times 34 \times 1^2} = 220$ deg. per min. That is, after being drawn this glass rod must have been cooled through the annealing range at a rate of about 200 deg. C. per minute. It is of interest to note that, according to equation (23) the stress at the surface of this glass was $3.4 \times 220 = 750$ kg./cm.^{2}

When the cylinder is viewed in a direction normal to the axis the problem is much more complicated. In this case the observed path difference is due to the axial stress and to the components (in a direction normal to the line of sight and to the axis) of the radial and tangential stresses. Performing the necessary substitutions and integrating along a chord, we find that

$$\frac{\delta}{N} = b - b^3 + \sqrt{1-b^2}\left(\frac{2}{3} + \frac{b}{2} - \frac{8b^2}{3}\right) + \left(-\frac{b}{2} + \frac{b^3}{4}\right) \ln \frac{1+\sqrt{1-b^2}}{1-\sqrt{1-b^2}} \tag{30}$$

in which δ is the path difference along a chord whose distance from the centre is x; b is equal to x/a, a being the radius; and

$$N = \frac{\alpha\, hBa^3}{8(e-f)\kappa}$$

In Fig. XIV. 2 is shown the graph of equation (30). A qualitative check on the validity of this equation was obtained by placing a strained glass rod in a square glass jar, surrounding the rod with liquid of the same refractive index and viewing it between crossed nicols. The sign of the path difference is such that near the middle of the strained rod α is normal to the axis.

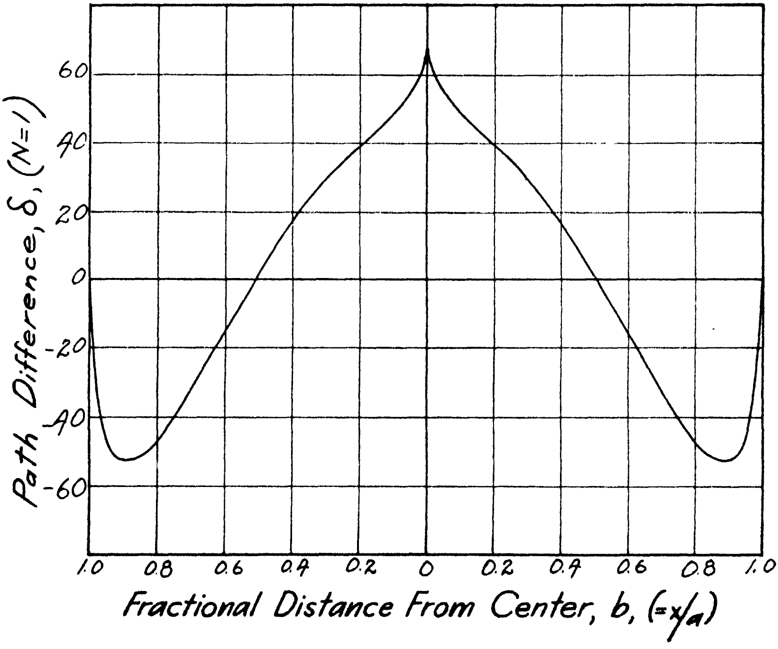

FIGURE XIV. 2.—The Optical Path Difference when a beam of light passes through a strained cylindrical rod in a direction normal to the axis. After Adams and Williamson.

Sphere.—The path differences in this case are due to both the radial and the tangential stresses, and the equation which resembles that for the cylinder viewed normal to the axis, is as follows:

$$\frac{\delta}{N} = -\frac{1}{3} + b - \frac{2}{3}b^3 + \sqrt{1-b^2}\left(\frac{1}{3} + \frac{b}{2} - \frac{4b^2}{3}\right) + \left(-\frac{b}{2} + \frac{b^3}{4}\right) \ln \frac{1+\sqrt{1-b^2}}{1-\sqrt{1-b^2}} \qquad (31)$$

in which

$$N = \frac{2\alpha\, hBa^3}{15(e-f)\kappa}$$

The remaining symbols have the meanings already explained; γ is always in the radial direction. This equation was qualitatively verified by observing Prince Rupert drops immersed in a liquid of the same refractive index.

Chapter XV

The Hardness of Glass

Hardness is a complex property which has not as yet received a satisfactory theoretical treatment. Because of the consequent uncertainty, the experimental methods proposed give results which are discordant, which are expressed in arbitrary and unrelated units, and which do not necessarily measure the property usually meant by the term hardness. The fundamental idea associated with hardness is that when we feel a substance, or press it with our fingers, it does not deform. The term "hard" is similar to many other technical terms which are also a part of every-day speech in that the usual and qualitative meaning is familiar and useful, but the quantitative specification in terms capable of measurement is difficult, if not impossible.

The most generally used criterion of relative hardness is the ability of a harder substance to scratch a softer one, and this criterion forms the basis of the well-known Mohs' scale, widely used in mineralogy. In this scale, glass occupies a position intermediate between apatite (5) and quartz (7), some glasses being scratched by, others scratching, orthoclase (6). Auerbach, however, found some flints to be softer than apatite, and a borosilicate crown harder than quartz. The matter is further complicated by the fact that the scratching test is not decisive, as Auerbach found that each one of a series of glasses ranging from the softest flints to the hardest borosilicate crown scratched every other one.

The method of Auerbach,[1] based on a theoretical investigation by Herz,[2] is typical of the more elaborate methods of hardness determination. If two surfaces in contact, one spherical, the other plane, both of the same composition and isotropic, are subjected to a pressure P, the surface of contact will be a portion of a sphere of radius $2r$, where r is the radius of the original sphere. The boundary of the surface of contact is a circle of diameter d, determined by the relation $E' = \frac{E}{(1-\sigma^2)} = \frac{12Pr}{d^3}$ in which σ and E are Poisson's ratio and Young's modulus, respectively. The ratio $E/(1-\sigma^2)$ is evidently a constant for a given glass, and Auerbach named it the indentation modulus, denoted by the symbol E'. The ratio Pr/d^3 involves quantities which

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[1] Auerbach, F., *Ann. Physik Chem.*, **53**, 1000 (1894).

[2] Herz, F., *J. reine Angen Math.*, **92**, 156 (1882).

can be determined by experiment. The method of experiment used by Auerbach was to press a lens of known curvature against a plane-polished piece of the same glass, and to measure with a microscope equipped with a micrometer eyepiece the diameter of the circle of contact, which is seen as a round black spot. The values of E' so determined are given in Table XV. 1; the glass composition references are to Table III. 4. The determinations with varying load and with varying radius of curvature showed a satisfactory constancy, but values of Poisson's ratio, calculated with the aid of the known values of Young's modulus, do not agree with those determined by Straubel.

TABLE XV. 1—Hardness of Glass

After Auerbach

Table and No.	E' (kg./mm^2)	F' (kg./mm^2)	H (kg/mm.$^{\frac{5}{3}}$)
III. 4, 40	5953	3.0	173
III. 4, 46	5588	4.1	183
III. 4, 43	5871	5.6	210
III. 4, 72	6811	4.6	217
III. 4, 48	4975	8.8	219
III. 4, 10	7107	4.5	223
III. 4, 19	5677	9.3	244
III. 4, 61	7792	6.4	266
III. 3, 5	7532	6.9	267
III. 4, 7	6796	9.0	272
III. 4, 1	7599	7.4	274
III. 4, 64	6197	11.6	278
III. 4, 69	8192	9.7	316

The indentation modulus so determined, which is essentially dependent on Young's modulus, was not found to bear any simple relation to the hardness, as determined by the scratching test. In carrying out the experiments, it was found that the limiting pressure which could be applied to the lens without the formation of a crack was proportional to the radius of curvature ρ, and thus was a characteristic constant of the glass. This constant was denoted by F', and if the limiting pressure be denoted by P', it is determined by the relation

$$F' = P'/\rho.$$

It was further empirically found that, though this new quantity itself bore no relation to the hardness, the latter was represented by the relation

$$H = \frac{1}{\pi}\sqrt[3]{\frac{3}{2}(E')^2F'}.$$

The values of F' and of H, so determined, are included in Table XV. 1. On the same scale, the hardness of fluorspar is 110; of apatite, 237; of adularia (orthoclase), 253; and of quartz, 308.

Bailey[3] made a careful study of the mechanics of scratching a glass surface. If two pieces of glass are rubbed together immediately after they have cooled from the molten condition, the coefficient of friction is greater than unity, and a visible scratch, confined to the upper layer, will be produced even when the rubbing pressure is very small. The finely powdered material which has been removed adheres so firmly to the powdered surface that it cannot be washed off with soap and water.[4]

The freshly cooled surface is quickly altered, so that the coefficient of friction drops to a low figure, and considerable pressure is required to start surface injury when two pieces are rubbed together. Powdered glass will be formed on the surface, but below it there are many incipient conchoidal fractures.

The speed of rubbing greatly influences the type of scratch. Slow scratching results in abrasion, as well as in some splintering. More rapid scratching results in a heating effect, which causes softening of either the scratching edge, if it is a material with low softening point, or the scratched surface, if the scratching point is of high softening point.

The ability of a material to resist grinding is a measure of its work-absorbing power, rather than of its hardness. True hardness depends upon mechanical properties, notably Poisson's ratio, and tensile strength. Glass is a material which does not show plastic flow, and when a load is applied by a point or ball which exceeds the tensile strength, crushing takes place. Bailey developed a method for measuring scratch hardness based on the above considerations. In it a hardened steel ball $\frac{1}{8}$ inch in diameter is rolled over the surface under increasing load, until the surface is ruptured. The results are rapid and reproducible.

Another method of hardness determination is that of Lecrenier,[5] who determined the rate of removal of material by grinding, under constant standard conditions. His results by this method, expressed as the volume in cc. ground off per minute, are given in Table XIII. 2, together with the results of hardness tests by Auerbach's method on the same glasses. Lecrenier's method gives a valuable indication of that phase of hardness most directly applicable to those important uses of glass which necessitate grinding and polishing, and it is evident that it places the glasses in a different order from Auerbach's method, which gives an order different from that obtained in the scratching test.

Gehlhoff and Thomas[6] studied the scratching hardness of glasses

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[3] Bailey, J., *J. Am. Ceram. Soc.*, **20**, 42 (1933).

[4] The seizing of glass surfaces has been discussed by Hardy, W. B., and Hardy, J. K., *Phil. Mag.*, **38**, 32 (1919); Hardy, W. B., *Phil. Mag.*, **38**, 49 (1919); *ibid.*, **40**, 201 (1920).

[5] Lecrenier, A., quoted by Le Chatelier, H., "Kieselsäure und Silicate," 246, Leipzig, 1920.

[6] Gehlhoff, G., and Thomas, M., *Zeit. tech. Physik*, **7**, 105 (1926).

derived from the two-component glass 0.18 Na_2O, 0.82 SiO_2 by replacing SiO_2 by one of the oxides Na_2O, K_2O, MgO, CaO, BaO, ZnO, PbO, B_2O_3, Al_2O_3, or Fe_2O_3. The method used was that of Marten, in which the surface of the glass is scratched by a diamond point of definite shape and under constant load, and the hardness is expressed as the reciprocal of the width of the crack in millimeters. The load used was 20 g., and the scratches ranged from 0.0039 to 0.0091 mm. wide. The results are summarized in Fig. XV. 1.

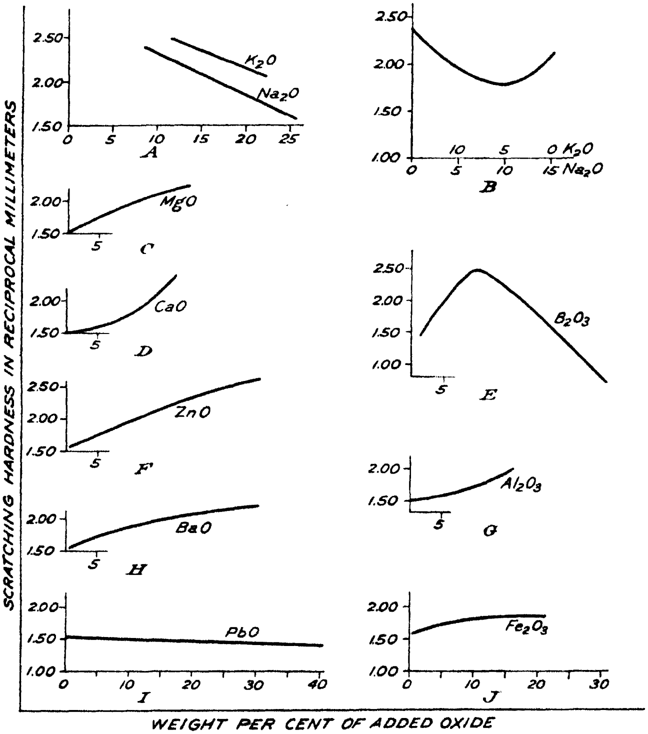

FIGURE XV. 1.—Scratching Hardness of Some Experimental Glasses. After Gehlhoff and Thomas.

Parmelee and Lyon[7] measured scratch hardness with a diamond point. The point, formed by planes at an angle of 130°, was loaded with different weights, and was moved at a constant rate of 2.7 mm. per minute across the surface of a glass sample cooled in air. The widths of the scratches were measured, and the apparatus was calibrated in terms of Mohs' scale with fluorite, apatite, orthoclase and quartz.

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[7] Parmelee, C. W., and Lyon, K. C., *Glass Ind.*, 17, 191 (1936).

The compositions and the hardness of the glasses studied and the values obtained in the calibration with minerals are in Table XV. 2.

Schmidt and Gronow[8] used a pendulum measure of hardness. A pendulum with a cutting edge of Widia metal was made to swing over a test-piece, and the work done in abrading the specimen was obtained from the decrease in amplitude of the pendulum. No correlation was established with other methods of measuring hardness.

Pirani and Fehse[9] studied the rate of removal of glass by turning on a lathe, using a tool of Widia metal, and by the penetration of a drill. They were explicit in their statement that, although this was in a sense a measure of hardness, it had not been correlated with other measures, and gave specifically a resistance of the material to a special type of working.

TABLE XV. 2—Hardness of Some Experimental Glasses *

After Parmelee and Lyon

No.	SiO_2	Na_2O	MgO	CaO	Al_2O_3	Hardness
1	73.50	15.68	4.38	6.07	0.35	5.42
2	70.92	15.70	4.14	5.88	3.36	5.51
3	69.90	15.68	3.92	5.75	4.75	5.65
4	69.73	15.39	3.60	4.95	6.33	5.56
5	69.00	13.78	3.90	5.61	7.71	5.71
6	72.7	15.4		10.7	1.2	5.48
7	72.5	15.6		11.2	0.7	5.51
8	72.7	13.7		12.9	0.7	5.81
9	72.6	15.4		10.5	1.5	5.40
10	71.8	15.3		10.6	2.3	5.38
11	72.5	13.7		11.5	2.3	5.58
12	100					6.31

* Unit: Mohs' scale, as standardized with fluorite (4), apatite (5), orthoclase (6) and quartz (7).

Holland and Turner[10] compared the hardness of ordinary plate glass and toughened "Armourplate." There was an evident difference between the sounds made by the diamond in scratching the two; and a glazier's wheel did not seem to "bite" the toughened glass. The fresh diamond cut on the toughened glass was hardly visible, but after some hours splintering took place along the sides of the scratch, giving a channel-like appearance. In spite of the difference in the manner in which they received the scratches, the hardnesses of the two types were of the same order.

No satisfactory method of measuring the hardness of glass has been devised, because no definition of hardness which can be expressed in measurable quantities has been formulated. The resistance which a body offers to the complex distribution of stress over its surface, which

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[8] Schmidt, W., and Gronow, H. E. v., *Glastech. Ber.*, **14**, 23 (1936); *Glass Ind.*, **17**, 118 (1936).

[9] Pirani, M., and Fehse, A., *Glastech. Ber.*, **14**, 21 (1936); *Glass Ind.*, **17**, 117 (1936).

[10] Holland, A. J., and Turner, W. E. S., *J. Soc. Glass Tech.*, **19**, 221 (1935).

stress has partially deformed or destroyed the surface at the point of application, must of course depend on the factors which determine the distribution of stress, the elastic moduli and Poisson's ratio, and on the tensile strength. But the exact nature of the stress which yields to breakdown has defied analysis because of its very complexity. Moreover, the method and the rate of application of the stress play an important part in the result, a fact which is evident to anyone who has had experience in cutting glass with a diamond. When that resistance is measured, without precise knowledge of the stress distribution and its variation with the method of application, the result cannot be a property of the material, but rather is a complex function of many variables, some of which cannot be specified. At present, what hardness is, and how it can be measured are not known.

Chapter XVI

The Optical Properties of Glass*

INTRODUCTION

The property of being transparent to light is one of the first to be connoted by the name glass, and one of prime importance in a large proportion of the uses to which glass is put. In many of these uses, it is necessary only that glass shall transmit most of the incident light; in others, special and stringent requirements must be met. The requirements of lens designers made desirable the development of glasses having varying relations between refractive index and dispersion; and from the search for glass compositions which have such relations has come much of our knowledge of the effects of changes in the nature and properties of the constituents of glass.

Other needs have led to the development of glasses still more specialized in their properties. Glasses transparent to x-rays and to ultra-violet light are articles of commerce, as are glasses opaque to these wave-lengths. Glasses are available which are opaque to infra-red while transparent to the visible part of the spectrum; and in addition, there are colored glasses which are opaque to all but narrow spectral range. In this chapter are collected the data in regard to the action of glass on light.

Definitions and Units.

When radiant energy meets the boundary between one substance or medium and another, some of it is reflected, and the rest passes into the second substance, where some of it is absorbed, some transmitted. The velocity of transmitted radiation is generally different for different substances. For glass and other isotropic substances, the ratio of the velocity in vacuum (v_o) to that in the given substance (v) is called the refractive index (n) of the substance:

$$n=\frac{v_o}{v}.$$

This difference in velocity causes the path of an obliquely incident beam of light to be bent toward the normal to the surface at the point of

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* I take pleasure in expressing my gratitude to my colleague, Dr. H. E. Merwin, for assistance in the preparation of this chapter, and for use of Fig. XVI. 12 before its publication elsewhere.

incidence, in such a manner that the path taken is that which requires the minimum time. The angle between the normal to the surface and the incident ray is the angle of incidence i; that between the normal and the refracted ray, the angle of refraction r; and Snell's law states that the ratio of the sine of the angle of incidence to the sine of the angle of refraction is constant; the refractive index is the ratio of the velocity of light in the two substances. When the first medium is a vacuum, the constant ratio is the absolute refractive index; when the first medium is air, as is ordinarily the case, the absolute index is obtained[1] by multiplying the index in air by the absolute refractive index of air, which is 1.000275 at 15° C., 760 mm., for light of wave-length $\lambda = 589.3\ \mathrm{m}\mu$.

The absorption of energy may be substantially uniformly distributed throughout the visible spectrum, in which case the substance is not colored, but appears gray; or there may be more or less pronounced maxima of absorption in the visible region, resulting in colored glass. The change in the velocity with frequency of the radiant energy in colorless glass may be represented by a dispersion curve, in which the refractive index n is related to wave-length λ. The simplest equation is the Cauchy formula:

$$n = A + \frac{B}{\lambda^2},$$

which gives a fair representation in the visible spectrum for most glasses. A better representation is obtained with the Hartman formula,

$$n = n_o + \frac{\mathrm{c}}{(\lambda - \lambda_o)\alpha},$$

in which λ_o, c, and α are constants, and the value of α ranges from 1 to 1.2. The Ketteler-Helmholz dispersion formula, which is more general, is

$$n^2 = n_a{}^2 + \sum \frac{M_m}{\lambda^2 - \lambda^2{}_m},$$

in which n is the refractive index for wave-length λ; $n\alpha$ is the index for infinitely long wave-lengths, and is equal to the square root of the dielectric constant K; and $\Sigma\lambda_m$ are the wave-lengths of the absorption bands, for each of which there is an empirical constant M_m. Thus this dispersion formula appears to have theoretical justification; and that the shape of the dispersion curve is determined by the presence of absorption bands in the ultra-violet and infra-red appears plausible. In no case, however, not even for silica glass, has the dispersion curve been completely correlated with known absorptions, and for all practical purposes the various dispersion formulas may be regarded as

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[1] Tilton, L. W., *J. Research Natl. Bur. Standards*, **14**, 392 (1935), gives a discussion of the standard conditions of refractometry.

empirical equations, the constants of which are to be evaluated from measurements of refractive index.

In passing through the medium, some of the energy is usually absorbed. The rate of absorption is proportional to the intensity, which results in the law:

$$I_t = I_o e^{-al}$$

in which I_t and I_o are the intensities of the transmitted and incident radiation, l is the thickness, and e the base of natural logarithms. The constant a, called the absorption modulus, is a function of the frequency; and, since the intensity of the radiation is proportional to the square of the amplitude,

$$I = I_o e^{\frac{-4\pi n\kappa l}{\lambda_0}} = I_o e^{\frac{-4\pi K l}{\lambda_0}}$$

in which n is the refractive index, λ_0 the wave-length in vacuum, κ a constant called the absorption index, and $K (= n\kappa)$ a constant called the absorption coefficient. The observed transparency, $\frac{I_t}{I_o}$, includes the loss by reflection R from each of the two surfaces; the corrected transparency is the observed transparency divided by $(1 - R)^2$.

"Bunsen's extinction coefficient" is the reciprocal value of that thickness which a layer must have in order that the light which passes through it shall be weakened by absorption to one-tenth the intensity of the light falling on it. If the coefficient is denoted by E,

$$E = \frac{\log I}{d},$$

where I is the intensity of the light which passes through thickness d, and the intensity of the light source is taken as unity.

TABLE XVI. 1—Designation, Source and Wave-length of Spectral Lines used in Spectrometric Measurements

Source	Hg	Hg	H	H	He	Hg
Designation	*h*	*g*	*G'*	F		*e*
Wave-length (mμ)	404.7	435.8	434.1	486.1	492.2	546.1

Source	Na (mean)	He	H	He	K (mean)
Designation	*D*	*d*	*C*	*b*	*A'*
Wave-length (mμ)	589.3	587.6	656.3	706.5	768.2

The refractive index is usually designated by the letter n, followed by a subscript indicating the wave-length of the light in vacuum at 15°; n_D indicates the refractive index for the (mean) D-line of sodium, $\lambda = 5893$ Ångstrom units $= 589.3$ mμ $= 0.5893$ μ. (One micron, μ, $= 10^{-3}$ mm.; 1 millimicron, mμ, $= 10^{-6}$ mm.; 1 Ångstrom unit $= 10^{-7}$ mm.) In optical glass catalogs it is customary to give the refractive indices for a group of spectral lines chosen by Abbé for the convenience with which they could be obtained for spectrometric work. The source, designation, and wave-length in vacuum at 15° C. of these lines is given in Table XVI. 1, together with some other lines which are being used to an increasing extent because of their present greater convenience.

Optical glass catalogs also give the "mean" dispersion, commonly designated by $(F\text{–}C)$, and other partial dispersions, as well as the dispersion ratios $\frac{(D\text{–}C)}{(F\text{–}C)}$, etc. Another number given under various names is the ratio

$$\nu = \frac{(n_D - 1)}{(n_F - n_C)}$$

Experimental Methods

The methods for measuring optical properties of glass are standard ones, described in detail in many text-books. They differ widely in the apparatus and experimental skill required and in the accuracy which can be obtained. Only those in common use for the measurement of the refractive index will be mentioned here.

Perhaps the simplest is the immersion method used by petrographers, in which the powdered material is placed in a liquid of known refractive index, and examined under a miscroscope in parallel light. If the surrounding liquid is of higher index than the glass, the system acts as a diverging lens, and on raising the objective above the focus a bright border will pass from the glass to the liquid; if the glass is of higher index, the bright border will appear to enter the glass; and on lowering the objective the reverse phenomena appear. The method is described and discussed in text-books [2] on petrographic methods. The same method is sometimes used on a large scale, especially for distinguishing between different types of glass.

The immersion method requires a set of liquids of known refractive index. The determination of refractive index to within ± 0.002 is rapid and simple. More accurate measurements can be made by the single variation methods of Merwin [3] and of Emmons,[4] or by the double variation method of Emmons.[5] The accuracy of microscopical methods for

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[2] Wright, F. E., "The Methods of Petrographic Microscopic Research," *Carnegie Institution of Washington Pub.* 158 (1911); *J. Wash. Acad. Sci.*, 4, 389 (1914); 5, 101 (1915). Johannsen, A., "A Manual of Petrographic Methods," McGraw-Hill, New York, 1914; Winchell, A. N., "The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals," 2nd ed., Wiley, New York, 1931; Larsen, E. S., and Berman, H., "The Microscopic Determination of the Non-opaque Minerals," *U. S. Geol. Survey Bull.*, 848 (1934); Chamot, E. M., and Mason, C. W., "Handbook of Chemical Microscopy," Wiley, New York, 1930; Rogers, A. F., and Kerr, P. F., "Thin-Section Mineralogy," McGraw-Hill, New York, 1933.

[3] Posnjak, E., and Merwin, H. E., *J. Am. Chem. Soc.*, 44, 1965 (1928). Tsuboi, S., *Mineralog. Mag.*, 20, 108 (1923); *J. Geol. Soc. Tokyo*, 32, 1 (1925).

[4] Emmons, R. C., *Am. Mineral.*, 13, 504 (1928).

[5] Winchell, A. N., and Emmons, R. C., *Am. Mineral.*, 11, 115 (1926). Emmons, R. C., *Am. Mineral.*, 13, 504 (1928); 14, 414, 441, and 482 (1929).

determining refractive index by immersion has been discussed by Saylor.[6]

More accurate measurements can be made also with one of the total reflection types[7] of refractometer, either the Abbé or the Pulfrich. Of the two, the Abbé refractometer, which is less accurate, at best gives values of refractive index reliable to a few units in the fourth decimal place. The values of dispersion may be dependable to within one-half a unit in the fourth place. The preparation of the sample is a little simpler than for the Pulfrich refractometer.

The Pulfrich refractometer is capable of giving values of refractive index accurate to better than one unit in the fourth decimal place, and of dispersion to one unit in the fifth place; but this accuracy is reached only by the most careful attention to details of calibration and manipulation. The sample of glass required is larger than for the Abbé instrument. It must have a polished surface two or three cm. long, that is accurately plane, at right angles to a small end surface. The intersection between the two polished faces must be free from bevel. A correction for slight deviation from a right angle usually is necessary.

The most accurate measurements are made with a spectrometer, using polished prisms. The methods, precautions and corrections in precise refractometry are treated in detail by Guild in the article in the "Dictionary of Applied Physics" cited above, and have been discussed also by Tilton.[8]

REFRACTIVE INDEX AND DISPERSION

Measurements of the refractive index, by which is usually meant the index for sodium light, $\lambda = 589.3$ mμ, have been made on (1) experimental glasses of simple compositions, to find the relation between composition and refractivity in systems of few components; and (2) multi-component and commercial glasses. There is much less information as to dispersion in simple glasses, but extensive measurements have been made on commercial optical glasses.

Experimental Glasses

Sulfur-selenium. Merwin and Larsen[9] prepared mixtures of these two elements for use as immersion media in the study of minerals of high refractive index, with the results given in Table XVI. 2. The melted elements are miscible in all proportions. The cooled mixtures, rich in

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[6] Saylor, C. P., *J. Research Natl. Bur. Research*, **15**, 277 (1935). See also Winchell, A. N., "The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals," Wiley, 2nd ed., New York, 1931.

[7] See the article "Spectroscopy and Refractometers" by Guild, J., in "A Dictionary of Applied Physics," **4**, 772, Glazebrook, R., editor, Macmillan, London, 1923.

[8] Tilton, L. W., *J. Research Natl. Bur. Standards*, **14**, 393 (1935).

[9] Merwin, H. E., and Larsen, E. S., *Am. J. Sci.*, **34**, 42 (1912).

selenium, remain as glasses for years; those very rich in sulfur may crystallize almost immediately on cooling or after some hours or days, according to the conditions of heating or cooling. The mixtures containing less than 50 per cent Se by weight, if heated on glass slips to near boiling and then cooled in air, crystallize more slowly and have slightly higher indices of refraction (0.01) than those which, after having crystallized, are scarcely melted and then cooled. By quenching some of the highly heated mixtures in water the index may be raised 0.05 above the values obtained by cooling in air. This effect probably is due to the presence of different amounts of the allotropic forms of molten sulfur, and it is an excellent example of the reality of the concept that the molecular condition of a liquid may change as a result of heat treatment.

TABLE XVI. 2—Refractive Indices of Some Sulfur-Selenium Mixtures

After Merwin and Larsen

% Se	n_{Li}	n_{Na}	% Se	n_{Li}	n_{Na}
0	1.978	1.998	57.0	2.200	2.248
9.0	2.000	2.022	64.0	2.250	2.307
17.6	2.025	2.050	70.0	2.300	2.365
25.0	2.050	2.078	75.0	2.350	2.423
31.8	2.075	2.107	80.0	2.400	2.490
37.5	2.100	2.134	87.7	2.500	2.624
43.2	2.125	2.163	93.8	2.600	2.755
48.2	2.150	2.193	99.2	2.700	2.90
53.0	2.175	2.220	100.0	2.716	2.92

TABLE XVI. 3—Dispersions of Two Sodium Borate Glasses and Boric Oxide*

After Morey and Merwin

Wave-length (mμ)	Source or Designation	$Na_2O \cdot 2B_2O_3$	$Na_2O \cdot 4B_2O_3$	B_2O_3
408.6	Hg	179	173+	169+
434.0	*G'*	145	140+	137
435.8	Hg	143	138+	135
486.1	*F*	98+	95+	93+
491.6	Hg	94+	91+	89+
546.1	Hg	61	59	58
587.6	He	41	40	39+
589.3	*D*	40	39	38+
656.3	*C*	15	15	15
667.8	He	11	11	11
706.5	He	0	0	0
768.2	*A'*			14+

* Values given are of $(n - n_{706.5}) \times 10^4$.

Boric oxide, B_2O_3. The refractive index of boric oxide has been studied by several observers, but there has not yet been a definite study of the removal of water and its effect, and of the effect of various annealing treatments on the refractive index.[10] Bedson and Williams[11] found the refractive index n_D, to be ± 1.463. Jenckel[12] found $n_D = 1.45766$ for a chilled glass. Wulff and Majumdar[13] made a careful study of the removal of water and the effect of annealing, and found the index to range from 1.4502 to 1.4633, according to the preparation of the sample. The best value of the index of B_2O_3 is probably 1.4582, which was obtained by them on a material heated 48 hours in a vacuum, and cooled during 13 hours. Unfortunately, the pertinent details were not given. Morey and Merwin[14] found 1.458 for n_D, together with the refractive dispersions given in Table XVI. 3. Measurements were made by the minimum deviation method on prisms of a few grams of glass cooled in air from fusion, and protected from filming by oil and cover glasses.

SiO_2. Sosman[15] discussed the optical properties of silica glass, and gave a table, reproduced as Table XVI. 4, showing the most probable values of the refractive indices at 18° in air at the same temperature, for light of wave-lengths from 185 to 795 mμ.

TABLE XVI. 4—Most Probable Values of the Refractive Index of Silica Glass at Various Frequencies, at 18°, in Air at Same Temperature

After Sosman

Radiating element	Wave-length in air at 15° (mμ)	N	Radiating element	Wave-length in air at 15° (mμ)	N
Al	185.467	1.574 36	Hg	404.656	1.469 68
Al	193.583	1.599 99	H	434.047	1.466 90
Zn	202.55	1.547 27	Hg	435.834	1.466 75
Cd	214.439	1.533 86	Cd	467.815	1.464 35
Cd	219.462	1.529 07	Cd	479.991	1.463 55
Cd	226.503	1.523 08	H (*F*) ...	486.133	1.463 18
Cd	231.288	1.519 41	Cd	508.582	1.461 91
Au	250.329	1.507 45	Cd	533.85	1.460 67
Cd	257.304	1.503 79	Hg	546.072	1.460 13
Cd	274.867	1.496 17	Na (mean)	589.29	1.458 45
Sn	313.412	1.485 94	Cd	643.847	1.456 74
Cd	340.365	1.478 67	H (*C*) ...	656.278	1.456 40
Ca	396.848	1.470 61	He	706.520	1.455 17
			Rb	794.763	1.453 40

GeO_2. Dennis and Laubengayer[16] measured the refractive indices of GeO_2 glass, using a Pulfrich refractometer, with the following results: $n_C = 1.6030$, $n_D = 1.6069$, $n_F = 1.6176$, $\nu = 41.6$. Transmission meas-

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[10] See the discussion of the density of B_2O_3, p. 227.

[11] Bedson, P. P., and Williams, C., *Ber.*, **14 B**, 2549 (1881).

[12] Jenckel, E., *Z. Elektrochem.*, **41**, 211 (1935).

[13] Wulff, P., and Majumdar, S. K., *Z Physik. Chem.*, *B*, **31**, 319 (1936).

[14] Morey, G. W., and Merwin, H. E., *J. Am. Chem. Soc.*, **58**, 2248 (1936).

[15] Sosman, R. B., "The Properties of Silica," Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

[16] Dennis, L. M., and Laubengayer, A. W., *J. Phys. Chem.*, **30**, 1510 (1926).

urements showed the glass to be opaque to wave-lengths of less than 0.325μ. There are no absorption bands between 0.8μ and 1.7μ.

B_2O_3-SiO_2. The refractive indices and densities for three glasses in this system were determined by Merwin and Morey,[17] with the results given in Table XVI. 5. The glasses were not annealed. The changes in density on annealing, shown in the same table, indicate that annealing would materially affect the refractive index, but experience has shown that the dispersion is not greatly affected by annealing.

TABLE XVI. 5—Optical Properties and Densities of B_2O_3-SiO_2 Glasses

After Merwin and Morey

Unannealed				Annealed	
SiO_2	n_d	*F-C*	*h-b*	*Density*	
27.7	1.454	0.0075	0.0163	1.879	1.902
31.2	1.454	0.0075	0.0163	1.884	2.039
62.5	1.456	0.0073	0.0155	2.026	

Na_2O-B_2O_3. Glasses in this system have been measured by Bedson and Williams,[11] Jenckel,[12] Wulff and Majumdar,[13] and Morey and Merwin.[14] Bedson and Williams found $n_D = 1.515+$ for "borax" glass. The measurements of Jenckel and of Wulff and Majumdar are combined in Table X. 2. Morey and Merwin found n_D for $Na_2O \cdot 2B_2O_3$ (69.14 wt. % B_2O_3) and $Na_2O \cdot 4B_2O_3$ (81.79 wt. % B_2O_3) to be 1.516 and 1.501, respectively. The agreement among the observers is not good, which is not surprising since the annealing treatment, of great importance in these glasses, was not the same. Morey and Merwin measured refractive dispersions for $Na_2O \cdot 2B_2O_3$ and $Na_2O \cdot 4B_2O_3$ glasses, with the results given in Table XVI. 3; the values for *C, D, F,* and *G′* were interpolated.

TABLE XVI. 6—Refractive Indices of Glasses in the System Li_2O-SiO_2

After Kracek

% SiO_2 by weight	Refractive index	% SiO_2 by weight	Refractive index
55.32	1.567 ± 0.003	79.00	1.538
66.78	1.557	80.08	1.535
74.88	1.546	80.93	1.533
76.64	1.543	82.29	1.529
77.93	1.540	84.98	1.522
		89.97	1.503

Li_2O-SiO_2. Kracek[18] measured the refractive indices of glasses in this system by the immersion method, with the results given in Table XVI. 6.

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[17] Unpublished results by Merwin, H. E., and Morey, G. W.

[18] Kracek, F. C., *J. Phys. Chem.*, **34**, 2641 (1930).

Na_2O-SiO_2. The refractive indices of glasses in this system have been measured by Peddle[19] (Table XVI. 9), Faick and Finn[20] (Table X. 4), and Morey and Merwin[21] (Table XVI. 11), and are included in Fig. X. 1. The measurements of Peddle were made on glasses melted in clay pots, and compositions were calculated from the proportions of the ingredients. The results of the other observers all refer to glasses of known composition. In general, the results of Morey and Merwin are highest, by amounts which can be accounted for by the lower temperatures and the longer times used for annealing.

K_2O-SiO_2. The measurements by Peddle,[19] included in Table XVI. 9, represent values extrapolated from the system K_2O-CaO-SiO_2.

The only direct measurements are about a dozen of Merwin and Morey,[17] which are included among those for K_2O-CaO-SiO_2 in Table XVI. 17. As potash increases in weight percentage in potash-silica glass, it is at first less effective than soda in soda-silica glass in raising the refractive index, but at about 56 per cent alkali the glasses have the same refractive index; a broad maximum of difference of 0.006 to 0.007 appears at 25 to 35 per cent alkali. Similarly the potash glasses are less dispersive, but the observed differences are proportionally about twice as great for the first 35 per cent and do not decrease at higher percentages. Thus, these glasses highest in potash have ν-values 12 to 15 per cent higher than corresponding soda glasses.

CaO-SiO_2. Larsen[22] gave the refractive index of CaO-SiO_2 glass for lithium, sodium and thallium ($\lambda = 535\ m\mu$) lights as: $n_{Li} = 1.6241$; $n_{Na} = 1.6280$; $n_{Tl} = 1.6317$. Measurements were made on prisms by the minimum deviation method, with a probable error of ± 0.0003. The composition was correct to 0.3 per cent; the thermal history of the samples was not mentioned. Eskola[23] gave for the same glass: $n_F = 1.635$; $n_{Tl} = 1.631$; $n_D = 1.628$; $n_C = 1.625$. Morey and Merwin[21] gave refractive indices for five glasses in this binary system, which are included in Table XVI. 11.

PbO-SiO_2. Table XVI. 7 contains the optical properties and the density of some glasses made to belong to this system, but containing small amounts of alkali oxide. They represent unpublished war-time data from the Geophysical Laboratory; the glasses were prepared by Olaf Andersen; the compositions were determined by analysis of the glasses, or by analysis of the ingredients, or by difference, including alumina, by E. T. Allen, R. H. Lombard, E. Posnjak, and E. G. Zies; the

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[19] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 3 (1920).

[20] Faick, C. A., and Finn, A. N., *J. Am. Ceram. Soc.*, **14**, 518 (1931); *Bur. Standards J. Research*, **6**, 993 (1931); (RP 320).

[21] Morey, G. W., and Merwin, H. E., *J. Optical Soc. Am.*, **22**, 632 (1932).

[22] Larsen, E. S., *Am. J. Sci.*, **28**, 263 (1909).

[23] Eskola, P., *Am. J. Sci.*, **4**, 331 (1922).

optical properties and the densities were determined by O. Andersen and H. E. Merwin.

SrO-SiO_2 and BaO-SiO_2. Eskola[23] measured the refractive indices for the *F*, *D*, and *C* lines, and for *Tl* ($\lambda = 535$ mμ) by Merwin's improvement of the immersion method, with the results given in Table XVI. 8.

TABLE XVI. 7—Optical Properties and Densities of Glasses in the System PbO-SiO_2

After Merwin and Andersen

No.	Composition SiO_2	Na_2O	K_2O	PbO	Density	n_D	$n_D - n_C$	$n_F - n_C$	$n_G - n_C$	ν
1	70.5	0.3	20.0	9.2		1.5071	.00027	0.0092	0.0145	55.1
2	65.2	0.3	14.7	19.4		1.5286	30+	106+	169+	49.7
3	55.1	0.4	15.1	29.0		1.5629	38	132	211	42.7
4	45.0	0.8	10.2	43.8	3.553	1.6157	48+	169	272	36.4
5	39.7	1.2	10.0	49.3	3.795	1.6450	55	194	313	33.2
6	38.1	9.4		52.5		1.6694	60	214	346	31.3
7	35.1	1.2	9.7	53.4	4.023	1.6754	62	220	356	30.7
8	40.4	(1.5)		58.1	4.181	1.6788	59	213	344	31.9
9	35.4	1.5	5.0	58.1	4.190	1.6836	61	218	352	31.4
10	34.4	1.8		63.8	4.593	1.7278	70	251	408	29.0
11	29.3	(1.8)		68.9	5.001	1.7800	83	295	483	26.4
12	24.9	1.6	0.2	72.9	5.395	1.8342	96	348	572	24.0
13	24.4	(2.0)		73.6	5.450	1.8415	98	355	585	23.7
14	18.6[p]	1.6	3.7	76.1	5.797[r]	1.8876	122	445	743	19.9
15	20.0	1.6		77.9	5.884	1.9060	118	431	718	21.0
16	19.7	(1.7)		78.6	5.944	1.9152	122	442	735	20.7
17	20.5	0.4		78.9	6.017	1.9163	120	436	720	21.0
18	17.4	2.0		80.6	6.170	1.9543	138	504	845	18.9
19	15.2	2.3		82.6	6.367	1.9929	154	574	967	17.3
20	(11.7)	(1.7)		86.6	6.84_0*	2.0789	190	718	1228	15.0_8
21	7.99	1.83		90.04	7.21[s]	2.179	256	988	176_0	11.9_4

[p] Composition from mixture of two analyzed glasses.
[r] Not annealed.
[s] Extrapolated.
* Subscript numbers are less precise.

Na_2O-BeO-SiO_2. Lai and Silverman[24] measured the refractive index n_D of glasses in this system, using an Abbé refractometer. Batch compositions were given for small melts in clay crucibles. The results are in Table X. 6. Comparison with glasses of similar molecular composition, but containing MgO or CaO in place of BeO shows that the refractive indices of the beryllium glasses are intermediate between those of magnesia and lime.

Becker[25] studied three series of glasses (Table X. 7.) In the *A*-series, to a parent glass, made to have the composition $Na_2O \cdot 3SiO_2$ but containing: SiO_2, 73.60; Na_2O, 25.01; CaO, 0.37; Al_2O_3, 0.69; Fe_2O_3, 0.06, beryllium oxide was added in steps of 0.2 mole, up to 1.8 moles. In the *B*-series, the glasses had the composition $(1 - x)$ Na_2O, xBeO, $3SiO_2$; and

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[24] Lai, C. F., and Silverman, A., *J. Am. Ceram. Soc.*, **11**, 535 (1928).
[25] Becker, C. A., *Sprechsaal*, **67**, 137, 152, 169, 185, 203, 216, 233, 250 (1934).

in the *V*-series 0.25 and 0.5 mole of BeO, MgO, CaO, or Al_2O_3 were added to the parent glasses.

Na_2O-CaO-SiO_2. The most complete studies of the relation between composition and optical properties have been made in this system by Peddle, by Clarke and Turner, by Faick and Finn, and by Morey and Merwin. The range of compositions studied by each of these observers is given in Fig. X. 3.

TABLE XVI. 8—Optical Properties and Densities of Glasses Containing Strontium Oxide or Barium Oxide

After Eskola

Composition			n_F	n_{Tl}	n_D	n_C	Density
SrO	SiO_2						
46.2	53.8	($SrO \cdot 2SiO_2$)	1.591	1.587	1.584	1.581	3.201
50	50		1.598	1.595	1.5915	1.589	
60	40		1.632	1.627	1.624	1.621	
63.2	36.8	($SrO \cdot SiO_2$)	1.640	1.636	1.632	1.629	3.537
67	33		1.652	1.648	1.644	1.641	
BaO							
45	55		1.576	1.571	1.5665	1.5635	
50	50		1.593	1.598	1.585	1.582	3.441
56	44	($BaO \cdot 2SiO_2$)	1.617	1.612	1.6085	1.605	
65	35		1.653	1.648	1.645	1.641	
$CaO \cdot SiO_2$	$SrO \cdot SiO_2$						
100	0		1.635	1.631	1.628	1.625	
87.5	12.5		1.634	1.630	1.6265	1.6245	
62.5	37.5		1.634	1.630	1.627	1.625	
43.75	56.25		1.636	1.633	1.628	1.625	
37.5	62.5		1.637	1.632	1.628	1.626	
$CaO \cdot SiO_2$	$BaO \cdot SiO_2$						
75	25		1.643	1.638	1.6345	1.6305	
60	40		1.649	1.6435	1.6395	1.636	
50	50		1.6525	1.647	1.644	1.640	
40	60		1.658	1.653	1.649	1.645	3.633
25	75		1.6655	1.6605	1.657	1.653	
0	100*		(1.681)*	(1.675)*	(1.672)*	(1.668)*	

* Extrapolated.

Peddle's results[26] (Table XVI. 9) refer to two series of glasses which represent addition of CaO to the compositions $100SiO_2 + 40$ (or 20) Na_2O. Some measurements were made on glasses in which SiO_2 was held constant at 70, 65, or 60 per cent, while the proportions of Na_2O and CaO were altered (series 171). All compositions were calculated from the batches melted, but four analyses were made showing the impurities (in one case 1.35 per cent Al_2O_3 and corresponding SiO_2) introduced by attack on the small clay pot during melting. The method of annealing was not mentioned.

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[26] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 20, 83 (1920).

TABLE XVI. 9—Optical Properties and Densities of Glasses Studied by Peddle

No.	x	Weight per cent	Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
		Series 162[1]—100 moles SiO_2 : x moles Na_2O				
	Na_2O	SiO_2				
A	20	83.33	2.353	1.4851	790	
B	30	76.92	2.413	1.4952	835	
C	40	71.43	2.457	1.5015	875	
D	50	66.77	2.495	1.5056	909	
E	60	62.50	2.521	1.5090	937	
F	70	58.82	2.535	1.5118	962	
G	80	55.56	2.544	1.5139	983	
H	90	52.63	2.555	1.5155	1002	
K	100	49.91	2.560	1.5168	1017	
		Series 84—100 moles SiO_2 : x molcs K_2O. (Extrapolated)				
A	20	(76)	2.388	1.4937	809	
C	40	(61)	2.465	1.5073	888	
		Series 163[2]—100 SiO_2 : 40Na_2O : xCaO				
	CaO	CaO				
A	5	3.22	2.412	1.5110	898	269
B	10	6.23	2.533	1.5189	918	274
C	15	9.07	2.559	1.5259	938	279
D	20	11.73	2.584	1.5327	955	283
E	30	16.62	2.629	1.5442	984	289
F	40	21.00	2.667	1.5540	1010	295
		Series 165[2]—100SiO_2 : 20Na_2O : xCaO				
A	5	3.73	2.412	1.4970	815	245
B	10	7.19	2.458	1.5088	841	252
C	15	10.41	2.499	1.5192	865	258
D	20	13.42	2.537	1.5279	888	264
E	30	18.86	2.603	1.5435	934	276
F	40	23.65	2.659	1.5573	980	287
		Series 167[3]—100SiO_2 : 40K_2O : xCaO				
A	5	2.78	2.488	1.5125	901	270
B	10	5.40	2.513	1.5179	914	272
C	15	7.89	2.535	1.5229	927	275
D	20	10.26	2.555	1.5277	938	278
E	30	14.63	2.594	1.5379	960	282
F	40	18.61	2.630	1.5475	978	286
		Series 168[3]—100SiO_2 : 20K_2O : xCaO				
A	5	3.42	2.420	1.5011	828	248
B	10	6.61	2.450	1.5081	846	253
C	15	9.59	2.478	1.5151	865	258
D	20	12.40	2.505	1.5223	883	262
E	30	17.51	2.555	1.5355	922	272
F	40	22.06	2.601	1.5491	958	281
		Series 175[4]—100SiO_2 : 13.16K_2O : xCaO				
A		3.73	2.360	1.4943	783	
B		7.19	2.397	1.5036	806	
C		10.41	2.432	1.5127	829	
D		13.42	2.472	1.5211	852	
E		18.86	2.542	1.5371	898	
F		23.65	2.607	1.5508	945	

TABLE XVI. 9—(*Continued*)

No.	x	Weight per cent	Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
		Series 169[4]—$100\mathrm{SiO_2} : 20\mathrm{Na_2O} : 20\mathrm{K_2O} : x\mathrm{CaO}$				
A	5	2.97	2.502	1.5115	900	269
B	10	5.76	2.529	1.5186	915	273
C	15	8.41	2.554	1.5255	933	277
D	20	10.90	2.574	1.5314	948	281
E	30	15.50	2.619	1.5428	977	287
F	40	19.65	2.657	1.5528	1002	293
		Series 170[4]—$100\mathrm{SiO_2} : 10\mathrm{Na_2O} : 10\mathrm{K_2O} : x\mathrm{CaO}$				
A	5	3.56	2.415	1.4992	823	247
B	10	6.88	2.450	1.5086	843	252
C	15	9.96	2.485	1.5177	865	258
D	20	12.85	2.523	1.5253	884	263
E	30	18.11	2.585	1.5401	928	274
F	40	22.78	2.626	1.5528	966	283
		Series 180[6]—$100\mathrm{SiO_2} : 40\mathrm{Na_2O} : x\mathrm{PbO}$				
	PbO	PbO				
A	5	11.62	2.710	1.5299	1069	310
B	10	20.82	2.912	1.5558	1246	360
C	15	28.28	3.112	1.5761	1390	401
D	20	34.46	3.282	1.5927	1522	437
E	30	44.09	3.5343	1.6219	1757	501
F	40	51.26	3.756	1.6472	1980	560
		Series 181[6]—$100\mathrm{SiO_2} : 20\mathrm{Na_2O} : x\mathrm{PbO}$				
A	5	13.34	2.628	1.5186	990	289
B	10	23.54	2.911	1.5448	1191	345
C	15	31.59	3.152	1.5691	1351	390
D	20	38.11	3.368	1.5930	1496	431
E	30	48.01	3.690	1.6272	1767	505
F	40	55.19	3.940	1.6571	1984	563
		Series 182[7]—$100\mathrm{SiO_2} : 40\mathrm{K_2O} : x\mathrm{PbO}$				
A	5	10.20	(2.681)	(1.5290)		
B	10	18.50	(2.868)	(1.5510)		
C	15	25.40	(3.043)	(1.5710)		
D	20	31.23	3.175	1.5910	1543	443
E	30	40.52	3.474	1.6230	1543	519
F	40	47.60	3.728	1.6508	2037	555
		Series 183[7]—$100\mathrm{SiO_2} : 20\mathrm{K_2O} : x\mathrm{PbO}$				
A	5	12.31	2.616	1.5201	1029	300
B	10	21.94	2.849	1.5480	1200	348
C	15	29.65	3.089	1.5707	1372	396
D	20	39.97	3.290	1.5941	1514	436
E	30	45.74	3.640	1.6284	1794	511
F	40	52.91	3.942	1.6596	2022	585
		Series 184[8]—$100\mathrm{SiO_2} : 20\mathrm{Na_2O} : 20\mathrm{K_2O} : x\mathrm{PbO}$				
A	5	10.83	(2.690)	1.5331	1078	313
B	10	19.56	2.888	1.5562	1260	364
C	15	26.72	3.080	1.5773	1411	406
D	20	32.71	3.248	1.5947	1550	445
E	30	42.16	3.507	1.6226	1808	515
F	40	49.30	3.731	1.6509	2029	574

TABLE XVI. 9—(*Continued*)

No.	x	Weight per cent	Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
Series 185[8]*—100SiO$_2$: 10Na$_2$O : 10K$_2$O : xPbO*						
A	5	12.77	(2.623)	(1.5180)	(1018)	(296)
B	10	22.66	2.884	1.5453	1198	347
C	15	30.54	3.126	1.5692	1362	394
D	20	36.93	3.339	1.5933	1503	433
E	30	46.76	3.676	1.6280	1781	509
F	40	53.95	3.952	1.6571	2006	570
Series 190[10]*—100SiO$_2$: 40Na$_2$O : xBaO*						
	BaO	BaO				
A	5	8.3	2.604	1.5155	920	273
B	10	15.3	2.738	1.5280	958	283
C	15	21.3	2.864	1.5404	985	291
D	20	26.5	2.966	1.5510	1013	299
E	30	35.1	3.134	1.5679	1055	310
F	40	41.9	3.248	1.5775	1084	319
Series 191[10]*—100SiO$_2$: 20Na$_2$O : xBaO*						
A	5	9.5	(2.557)	(1.5037)	(842)	(251)
B	10	17.4	2.708	1.5202	885	263
C	15	24.0	2.853	1.5357	921	273
D	20	29.7	2.987	1.5483	957	284
E	30	38.8	3.203	1.5698	1015	300
F	40	45.8	3.407	1.5895	1067	315
Series 192[11]*—100SiO$_2$: 40K$_2$O : xBaO*						
A	5	7.2	2.619	1.5195	912	269
B	10	13.5	2.718	1.5285	937	277
C	15	19.0	2.803	1.5381	962	283
D	20	23.8	2.904	1.5479	988	291
E	30	31.9	3.079	1.5644	1030	303
F	40	38.5	3.205	1.5757	1057	310
Series 193[11]*—100SiO$_2$: 20K$_2$O : xBaO*						
A	5	8.8	2.565	1.5080	844	251
B	10	16.2	2.681	1.5203	884	262
C	15	22.5	2.798	1.5317	922	273
D	20	27.9	2.922	1.5437	962	285
E	30	36.8	3.143	1.5652	1020	301
F	40	43.7	3.308	1.5838	1071	316
Series 194[12]*—100SiO$_2$: 20Na$_2$O : 20K$_2$O : xBaO*						
A	5	7.7	2.614	1.5170	904	267
B	10	14.4	2.753	1.5293	945	279
C	15	20.1	2.883	1.5414	976	287
D	20	25.1	3.001	1.5520	1003	295
E	30	33.5	3.161	1.5681	1046	308
F	40	40.2	3.302	1.5820	1083	317
Series 195[12]*—100SiO$_2$: 10Na$_2$O : 10K$_2$O : xBaO*						
A	5	9.2	2.562	1.5058	832	247
B	10	16.8	2.695	1.5199	880	261
C	15	23.3	2.821	1.5342	921	274
D	20	28.8	2.951	1.5476	961	284
E	30	37.7	3.175	1.5694	1017	300
F	40	44.7	3.349	1.5881	1073	316

TABLE XVI. 9—(*Continued*)

Series 200[14]*—*$5SiO_2 : (2 - x) Na_2O : xMgO$

No.	x	Weight per cent	Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
	MgO					
A	0.25		2.453			
B	0.375		2.448			
C	0.50		2.444			
D	0.625		2.439			
E	0.75		2.433			
F	1.00		2.421			

Series 171[6]

No.	Weight per cent				Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
	SiO_2	CaO	Na_2O	K_2O				
A	70	5	25	..	2.495	1.5128	896	258
E	70	5	..	25	2.430	1.5072	839	261
B	70	10	20	..	2.525	1.5231	905	269
W	70	10	10	10	2.509	1.5206	876	260
F	70	10	..	20	2.467	1.5175	852	253
C	70	15	15	..	2.542	1.5330	914	271
V	70	15	7.5	7.5	2.534	1.5307	882	261
G	70	15	..	15	2.503	1.5280	865	256
D	70	20	10	..	2.572	1.5423	923	272
T	70	20	5	5	2.563	1.5406	888	262
H	70	20	..	10	2.542	1.5385	878	259
K	65	15	20	..	2.588	1.5367	948	281
Z	65	15	10	10	2.569	1.5349	918	272
P	65	15	..	20	2.524	1.5296	900	266
M	65	20	15	..	2.516	1.5473	957	282
R	65	20	..	15	2.564	1.5410	913	269
N	60	15	25	..	2.605	1.5402	982	289
S	60	15	..	25	2.544	1.5320	935	275
L	60	20	20	..	2.637	1.5508	990	290
Y	60	20	10	10	2.616	1.5485	962	282
Q	60	20	..	20	2.584	1.5432	948	279

Series 186[8]

No.	SiO_2	PbO	Na_2O	Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
A	70	5	25	2.531	1.5092	898	266
B	70	10	20	2.610	1.5154	930	280
C	70	15	15	2.701	1.5197	1005	294
E	65	15	20	2.742	1.5298	1072	313
F	65	20	15	2.836	1.5349	1126	328
H	60	15	25	2.783	1.5419	1140	332
J	60	20	20	2.887	1.5475	1195	347
K	60	25	15	2.981	1.5517	1253	362
L	60	30	10	3.075	1.5568	1319	380
M	50	30	20	3.172	1.5822	1451	416
N	50	35	15	3.268	1.5869	1511	434
P	50	40	10	3.364	1.5915	1570	451
Q	40	40	20	3.458	1.6165	1700	488
R	40	25	15	3.561	1.6219	1764	501
S	40	50	10	3.665	1.6262	1828	519
T	30	50	20	3.742	1.6509	1955	553

TABLE XVI. 9—(*Continued*)

Series 187[8]

No.	Weight per cent			Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
	SiO_2	PbO	K_2O				
A	70	5	25	2.471	1.5023	818	243
B	70	10	20	2.546	1.5087	878	258
C	70	15	15	2.644	1.5197	1005	294
E	65	15	20	2.697	1.5248	998	292
F	65	20	15	2.774	1.5319	1063	310
H	60	15	25	2.712	1.5350	1071	312
J	60	20	20	2.819	1.5415	1128	328
K	60	25	15	2.917	1.5487	1203	349
L	60	25	15	3.010	1.5558	1263	364
M	50	30	20	3.092	1.5754	1378	397
N	50	35	15	3.189	1.5824	1442	415
P	50	40	10	3.275	1.5903	1510	434

Series 188[9]

No.	Weight per cent				Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
	SiO_2	PbO	Na_2O	K_2O				
B	70	10	10	10	2.570	1.5110	901	266
E	65	15	10	10	2.714	1.5265	1022	300
J	60	20	10	10	2.845	1.5434	1151	334
M	50	30	10	10	3.123	1.5778	1401	403
Q	40	40	10	10	3.427	1.6114	1651	474
T	30	50	10	10	3.742	1.6465	1904	541

Series 196[13]

No.	Weight per cent			Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
	SiO_2	BaO	Na_2O				
A	70	5	25	2.533	1.5078	892	264
B	70	10	20	2.593	1.5125	880	261
C	70	15	15	2.648	1.5168	867	264
E	65	10	25	2.632	1.5190	921	273
F	65	15	20	2.696	1.5236	911	271
G	65	20	15	2.773	1.5284	901	268
J	60	15	25	2.744	1.5295	946	279
K	60	20	20	2.815	1.5347	940	278
L	60	25	15	2.891	1.5403	933	277
M	60	30	10	2.971	1.5459	928	276
N	50	25	25	2.965	1.5506	1002	295
P	50	30	20	3.056	1.5572	1000	295
Q	50	35	15	3.132	1.5643	1002	296
R	50	40	10	3.227	1.5711	1003	297

Series 201[13]

No.	Weight per cent			Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
	SiO_2	BaO	K_2O				
A	70	5	25	2.486	1.5023	860	255
B	70	10	20	2.535	1.5055	842	250
C	70	15	15	2.579	1.5082	818	243
E	65	10	25	2.598	1.5127	890	264
F	65	15	20	2.632	1.5173	870	259
G	65	20	15	2.714	1.5221	860	256
J	60	15	25	2.687	1.5224	923	272
K	60	20	20	2.766	1.5278	911	270
L	60	25	15	2.850	1.5344	898	267
M	60	30	10	2.933	1.5402	884	263
N	50	25	25	2.917	1.5463	982	288

TABLE XVI. 9—(*Continued*)

Series 201[13]*—(Continued)*

No.	Weight per cent			Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
	SiO_2	BaO	K_2O				
P	50	30	20	3.004	1.5525	980	289
Q	50	35	15	3.083	1.5591	980	289
R	50	40	10	3.187	1.5652	983	291

Series 202[13]

No.	Weight per cent				Density	n_D	$(n_F - n_C)10^5$	$(n_D - n_C)10^5$
	SiO_2	BaO	Na_2O	K_2O				
A	70	5	12.5	12.5	2.528	1.5049	877	260
B	70	10	10	10	2.545	1.5086	865	257
C	70	15	7.5	7.5	2.634	1.5142	850	253
E	65	10	12.5	12.5	2.652	1.5185	907	269
F	65	15	10	10	2.705	1.5224	875	259
G	65	20	7.5	7.5	2.752	1.5263	886	263
K	60	20	10	10	2.834	1.5332	925	274
L	60	25	7.5	7.5	2.881	1.5835	915	272
M	60	30	5	5	2.949	1.5449	905	269
P	50	30	10	10	3.038	1.5566	988	292
Q	50	35	7.5	7.5	3.227	1.5637	988	292
R	50	40	5	5	3.234	1.5704	988	295

1. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 3 (1920).
2. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 20.
3. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 46.
4. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 59.
5. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 71.
6. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 299.
7. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 310.
8. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 320.
9. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 330.
10. Peddle, C. J., *J. Soc. Glass Tech.*, **5**, 201 (1921).
11. Peddle, C. J., *J. Soc. Glass Tech.*, **5**, 212.
12. Peddle, C. J., *J. Soc. Glass Tech.*, **5**, 220.
13. Peddle, C. J., *J. Soc. Glass Tech.*, **5**, 228.
14. Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 281 (1920).

Clarke and Turner[27] measured the refractive index and dispersion of a series of glasses which were used also for other measurements. The optical measurements are in Table XVI. 10. The compositions, which were determined by analysis, are in Table X. 3; and the range of compositions studied is shown in Fig. X. 3.

The results of Faick and Finn[28] are given in Table X. 4, which includes the annealing temperatures used by them. Compositions were determined by analysis. They considered that their values of refractive index were best represented by three straight lines, of the general formula

$$(n - 1) = aA + bB + cC,$$

in which A, B, and C represent the percentages by weight of SiO_2, Na_2O, and CaO, and a, b, and c are empirical constants having the following values in the indicated silica ranges:

Silica range (%)	a	b	c
50 to 59.5	0.004836	0.005491	0.007521
59.5 to 73.75	0.004785	0.005568	0.007598
73.75 to 100	0.004584	0.006127	0.007977

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[27] Clarke, J. R., and Turner, W. E. S., *J. Soc. Glass Tech.*, **4**, 111 (1920).

[28] Faick, C. A., and Finn, A. N., *J. Am. Ceram. Soc.*, **14**, 518 (1931).

TABLE XVI. 10—Optical Properties* of Glasses Studied at the Department of Glass Technology, University of Sheffield, Sheffield, England

Glasses Na_2O-CaO-SiO_2

No.	n_C	n_D	n_F	$n_{G'}$	γ
1	1.4949	1.4977	1.5066	1.5120	42.6
2	1.4982	1.5007	1.5068	1.5123	58.6
3	1.4996	1.5027	1.5083	1.5147	58.6
4	1.5016	1.5041	1.5102	1.5167	58.7
5	1.5038	1.5063	1.5124	1.5178	58.6
6	1.5060	1.5085	1.5146	1.5189	58.9
7	1.5084	1.5108	1.5171	1.5217	58.8
8	1.5101	1.5127	1.5188	1.5241	58.9
9	1.5128	1.5154	1.5215	1.5267	59.0
10	1.5142	1.5168	1.5229	1.5289	59.5
11	1.5164	1.5188	1.5250	1.5317	59.7
Trisilicate glasses Na_2O-Al_2O_3-SiO_2					
441	1.49406	1.49731	1.50271	1.50700	57.4
442	1.49350	1.49666	1.50204	1.50604	58.2
443	1.49284	1.49523	1.50109	1.50584	59.9
444	1.49232	1.49443	1.50052	1.50517	60.2
Glasses Na_2O-B_2O_3-SiO_2					
601	1.49868	1.50110	1.51375	1.52705	33.8
602	1.50875	1.51130	1.52372	1.53703	34.1
603	1.51361	1.51610	1.52855	1.54180	34.1
604	1.51582	1.51833	1.53058	1.54400	35.1
605	1.51881	1.52124	1.53384	1.54607	34.8
606	1.52277	1.52532	1.53746	1.55084	35.7
607	1.52023	1.52335	1.53506	1.54811	35.4
608	1.51940	1.52181	1.53421	1.54753	35.3
609	1.50199	1.50451	1.51284	1.51654	46.4
610	1.49322	1.49542	1.50271	1.50718	47.2
611	1.49037	1.49277	1.50109	1.50422	46.0
612	1.48695	1.48924	1.49765	1.50182	45.7
613	1.48541	1.48761	1.49631	1.50086	44.7
614	1.48292	1.48558	1.49381	1.49815	44.6
615	1.48234	1.48490	1.49314	1.49758	44.9
616	1.48550	1.48790	1.49603	1.50047	46.3
Glasses $(75.8 - x)$ SiO_2, xB_2O_3, $8.56CaO$, $6.86Na_2O$, $7.9K_2O$					
755	1.5073	1.5098	1.5156		61.1
755B	1.5082	1.5108	1.5166		60.8
755E	1.5207	1.5233	1.5291		62.3
755F	1.5223	1.5248	1.5306		63.2
755G	1.5239	1.5265	1.5323		63.0
755H	1.5260	1.5285	1.5343		63.7
755H	1.5270	1.5302	1.5353		63.9
755J	1.5300	1.5326	1.5379		67.4
755L	1.5321	1.5346			
755M	1.5326	1.5351	1.5408		65.3
755O	1.5303	1.5330	1.5386		64.2
Glasses $6SiO_2$, $(2 - x)Na_2O$, $xTiO_2$					
753a	1.50185	1.50458	1.51743	1.53098	32.3
753b	1.50428	1.50693	1.52002	1.53344	32.3

* Compositions are in Table X. 3.

TABLE XVI. 10—(*Continued*)

		Glasses $6SiO_2$, $(2-x)Na_2O$, $xTiO_2$			
753c	1.51092	1.51381	1.52693	1.54061	32.1
753d	1.52125	1.52434	1.53762	1.55114	32.0
753e	1.52710	1.53030	1.54377	1.55766	31.8
753f	1.53565	1.53911	1.55269	1.56675	31.7
		Glasses $6SiO_2$, $(2-x)Na_2O$, $xZnO$			
788a	1.49686	1.49975	1.50572	1.51077	57.06
788b	1.49874	1.50153	1.50751	1.51251	58.18
788c	1.49827	1.50181	1.50707	1.51232	57.02
788d	1.50217	1.50534	1.51118	1.51646	56.10
788e	1.49874	1.50162	1.50724	1.51232	59.00
788g	1.50484	1.50765	1.51350	1.51868	58.62
788g/2	1.50511	1.50793	1.51396	1.51915	57.40
788h/2	1.51575	1.50829	1.51424		59.88

TABLE XVI. 11—Optical Properties and Densities of Glasses in the System Na_2O-CaO-SiO_2

After Morey and Merwin

					$\times 10^{-3}$			$\times 10^{-3}$	$\times 10^{-4}$		$\times 10^{-4}$
No.	Na_2O	CaO	SiO_2	Observed $d^{20/4}$ annealed	Add to observed *d* to obtain *d* of curves	*d* increased by annealing	Observed n_D annealed	Add to observed *n* to obtain *n* of curves	*n* increased by annealing	Observed $F-C$	Add to observed $(F-C)$ to obtain $(F-C)$ of curves
0	....	....	99.90	2.203	0	0	1.458_5	0	0	$67._5$	0
1	5.00	....	95.00	2.240	+ 1	2	1.465_5	0	9	72	0
1a	10.00	....	90.00	2.291	0	5	1.474	− ½	10	$75._5$	− ½
2	3.90	5.70	(90.40)	2.310	+ 1	(5)	1.483	− ½	(10)	..	..
2a	6.00	4.00	90.00	2.311	− 2	4	1.480_5	0	6	$75._5$	− ½
3	11.83	....	(88.17)	....	..	..	1.476_5	0	8	$75._5$	+ ½
3x	13.87	....	86.13	2.329	0	9	....	..	..	..	..
3a	10.89	3.01	86.10	2.345	− 1	3	1.486	0	12	78	0
3b	8.00	6.00	86.00	2.355	+ 2	5	1.490_5	0	8	78	0
4	14.86	....	(85.14)	2.334	+ 4	2	1.481	0	0	$77._5$	1
5	9.21	7.58	83.21	2.389	+ 4	7	1.498_5	0	14	$80._5$	+1
5a	17.95	....	82.05	2.369	0	9	....	..	..	..	..
6	6.55	11.65	81.80	2.421	+ 1	6	1.507	+ ½	..	..	..
7	19.55	....	(80.45)	2.383	+ 1	8	1.490	− ½	10	$82._5$	− ½
8	16.98	5.01	78.01	2.432	0	6	1.503_5	0	..	85	−1
9	12.0	10.0	78.0	2.455	+ 1	6	1.511	+ ½	..	85	0
9a	22.54	....	77.46	2.414	− 1	9	....	..	..	..	..
10	14.93	8.01	77.06	2.456	0	6	1.510	0	..	$85._5$	0
11	12.85	11.03	76.12	2.485	− 3	7	1.517	0	11	87	− ½
12	8.90	14.99	76.11	2.497	+ 1	5	1.523	0	6	87	0
13	18.89	5.01	76.10	2.455	− 5	11	1.506	0	16	$85._5$	+ ½
14	6.18	17.96	75.86	2.505	+ 4	6	1.527_5	+1	..	88	− ½
15	18.64	5.76	75.60	2.468	−10	9	1.509	−1	15	..	

0. A clear bead made from quartz in an oxy-hydrogen flame had a density of 2.203. The clearest pieces of Day and Shepherd's glass (*Sci.*, 23, 670, 1906) had *d* 2.204. A disk of optical silica had *d* 2.206. Annealing these either at 700° or at 1000° increased *d* not more than 0.001. For Day and Shepherd's glass n_D 1.458_8. $(F-C)$ is from the literature. Cf. "The Properties of Silica," R. B. Sosman.

1. Almost free of bubbles and striae. Fined at 1650°, quenched in mercury.

1a, 2. Same; fined at 1620°, quenched in mercury.

3a. Same; fined at 1550°, quenched in mercury.

5. Milky after 15 minutes at 650°.

9. Last fining 1 hr. at 1500°, loss 0.03 per cent.

10. Fined 16 hr. at 1350°; lost 0.01 per cent.

13. Became opalescent and corners rounded at 600° for several hours, then annealed at 460°. Duplicate tests of changes in *n* and *d* agreed.

14. Liquidus 1438°; fined at 1475°; quenched in H_2O.

15. Clear glass after annealing but slightly striated; large piece used. *d* redetermined.

TABLE XVI. 11—(*Continued*)

No.	Na_2O	CaO	SiO_2	Observed $d^{20/4}$ annealed	Add to observed *d* to obtain *d* of curves ×10^{-3}	*d* increased by annealing ×10^{-3}	Observed n_D annealed	Add to observed *n* to obtain *n* of curves ×10^{-3}	*n* increased by annealing ×10^{-4}	Observed *F*−*C* ×10^{-4}	Add to observed (*F*−*C*) to obtain (*F*−*C*) of curves ×10^{-4}
16	4.48	20.23	75.29	2.535	− 7	..	1.533	+ ½	..	..	..
17	17.25	7.54	75.21	2.475	− 1	8	1.512	− ½	..	88	−1
18	24.81	....	(75.19)	2.429	+ 1	10	1.497$_5$	0	15	87	−1
19	25.00	....	(75.00)	2.431	0	10	1.497$_5$	0	12	86.$_5$	− ½
20	17.50	7.50	75.00	2.477	− 1	5	1.512$_5$	− ½	..	87	0
21	15.04	9.98	74.98	2.489	− 1	..	1.517	0	10	87.$_5$	0
22	(13.40)	11.64	74.96	2.495	+ 2	..	1.519	+ ½	..	88	− ½
23	10.08	14.97	(74.95)	2.506	+ 5	..	1.525	+ ½	..	87	+ ½
24	15.20	10.10	74.70	2.489	+ 2	14	1.517	+ ½	15	87	+ ½
25	15.28	10.03	74.69	2.492	− 1	..	1.517$_5$	− ½	..	86.$_5$	+1
26	(5.37)	20.25	74.38	2.532	+ 6	(10)	....	..	..	..	..
27	(5.46)	20.25	74.29	2.536	+ 3	14	1.534$_5$	+1	..	88.$_5$	+ ½
28	5.73	20.02	(74.25)	2.522	+16	10	1.532$_5$	+2½	4	89	0
29	12.82	12.98	74.20	2.509	+ 1	8	1.524	− ½	..	88.$_5$	− ½
30	18.48	7.34	74.18	2.484	− 6	9	1.513$_5$	− ½	12	88$_5$	−1
31	20.73	5.12	74.15	2.469	− 2	16	1.508$_5$	+ ½	15	87.$_5$	0
33	13.88	12.02	74.10	2.505	+ 1	7	1.522	0	..	88.$_5$	− ½
34	15.04	11.03	73.93	2.505	− 2	..	1.521	− ½		89	−1
36	7.32	19.04	73.64	2.541	0	5	1.535	0	..	90	− ½
37	12.95	13.44	73.61	2.518	− 1	..	1.526	− ½	..	88	+ ½
38	13.30	13.13	73.57	2.519	− 3	..	1.526	−1		89.$_5$	−1
39	16.42	10.02	73.56	2.501	0		1.519$_5$	− ½		88	0
40	(23.48)	3.07	73.45	2.461	0	13	1.505	+ ½	11	87	+ ½
41	21.71	5.00	73.29	2.474	− 1	6	1.509$_5$	0		88	0
42	13.81	13.02	73.17	2.519	0	7	1.525$_5$	− ½		88	+1
42a	22.84	4.01	73.15	2.470	− 2	8	1.508	− ½		87.$_5$	0
43	17.91	9.01	73.08	2.500	− 1	..	1.518	− ½	..	88.$_5$	0
44	27.32	....	(72.68)	2.449	0	11	1.500$_5$	0	..	89	−1½
45	11.82	16.03	72.15	2.546	− 2	9	1.533	− ½	..	90.$_5$	− ½
46	8.92	19.02	72.06	2.560	− 2	..	1.538$_5$	−1	..	92	−1
47	(21.66)	6.54	71.80	2.495	− 2	16	1.514	0	11	89	0
48	18.52	10.10	71.38	2.518	− 1	7	1.522	− ½	12	91	−1
49	(21.35)	7.54	71.11	2.499	+ 5	8	1.515$_5$	+1½	15	90	0
50	10.91	18.02	71.07	2.561	+ 2	5	1.537$_5$	0	..	92	− ½
50a	5.46	23.66	70.88	2.594	0	11	1.549	−1	10	93	− ½
51	29.20	....	(70.80)	2.459	+ 2	10	1.502	0	10	..	..
52	9.11	20.19	70.70	2.585	− 8		1.544	−2		93.$_5$	−1½
53	24.02	5.32	70.66	2.495	− 1	6	1.513	0	..	90	0
54	(13.78)	15.66	70.56	2.553	+ 2	10	1.533$_5$	0	15	91	+ ½
55	15.68	14.04	70.28	2.549	− 1	9	1.531$_5$	− ½	..	92	− ½
56	14.77	15.00	70.23	2.557	− 3	..	1.533$_5$	− ½		92.$_5$	−1
57	23.26	6.52	70.22	2.504	0	5	1.516	− ½		91	0
58	24.86	4.94	70.20	2.499	− 4	10	1.513	− ½	10	91	− ½
59	15.91	14.08	70.01	2.548	+ 3	7	1.531	+ ½	..	92	− ½
60	24.71	5.31	69.98	2.496	+ 3	3	1.513$_5$	0	10	91.$_5$	0
60a	(25.55)	4.61	69.84	2.503	− 8	14	1.514	−2	(15)	90.$_5$	+1
61	(17.23)	13.00	69.77	2.540	+ 6	12	1.528$_5$	+1	15	90.$_5$	+1
62	25.79	5.01	69.20	2.504	− 2	7	1.513$_5$	0	..	91.$_5$	0
63	5.56	25.40	(69.04)	2.609	+11	12	1.552$_5$	+2½	6	94	0
64	20.54	10.78	68.68	2.544	− 5	9	1.526$_5$	− ½	..	93	−1
65	20.90	10.84	68.26	2.543	0	7	1.527	− ½	..	92.$_5$	0
66	13.83	18.04	68.13	2.586	+ 2	6	1.541$_5$	0	..	94	− ½
67	24.95	7.00	68.05	2.520	0	5	1.518$_5$	+ ½		92.$_5$	0
68	22.10	10.14	(67.76)	2.543	− 2	..	1.525$_5$	0		..	..
68a	32.43	....	67.57	2.484	− 2	24					
69	19.64	13.03	67.33	2.561	+ 1	..	1.532	0		93	+ ½
70	(3.87)	28.84	67.29	2.655	+ 1	5	1.564$_5$	0		97	− ½
71	17.45	15.57	66.98	2.582	− 3	..	1.538	0		94	0
72	5.98	27.24	66.78	2.654	0	5	1.563	− ½	6	97	0

16, 26, 27, 28. These four glasses were all attempts to make a glass of approximately 5 per cent Na_2O, 20 per cent CaO, 75 per cent SiO_2. Liquidus temperature 1475°; hard to get homogeneous, and very difficult to quench, even in mercury, without devitrification. Final quenching in small lots in mercury. Distinctly opalescent when first prepared, not distinctly more so when annealed.

31. The first glass melted in this study; $Fe_2O_3+Al_2O_3=0.12$ per cent.

52. Fined at 1550°.

60. Distinctly opalescent after annealing, barely so before. Changes due to annealing accurately determined in duplicate.

63. Difficult to quench, even in mercury; opalescent, striated.

TABLE XVI. 11—(*Continued*)

					$\times 10^{-3}$			$\times 10^{-3}$	$\times 10^{-4}$		$\times 10^{-4}$
No.	Na_2O	CaO	SiO_2	Observed $d^{20/4}$ annealed	Add to observed d to obtain d of curves	d increased by annealing	Observed n_D annealed	Add to observed n to obtain n of curves	n increased by annealing	Observed $F-C$	Add to observed $(F-C)$ to obtain $(F-C)$ of curves
73	(12.44)	20.79	66.77	2.613	0	10	1.549	− ½	5	$94._5$	− ½
74	23.45	10.07	66.48	2.547	+ 1	5	1.526_5	0		94	− ½
75	(32.20)	1.34	66.46	....	..	..	1.506_5	+1½	(10)	91	+1½
76	18.69	14.91	66.40	2.581	− 2	..	1.537	0		$94._5$	0
77	33.86	....	66.14	2.491	0	6	1.506	0	(5)	..	
78	17.80	16.04	66.16	2.591	− 2	..	1.540	0		$94._5$	0
79	18.95	15.06	65.99	2.584	0	..	1.538	0		..	
81	19.15	15.00	65.85	2.586	− 3	10	1.538	0		..	
82	9.07	25.28	65.65	2.656	− 0	16	1.559	+ ½	15	97	0
83	16.64	17.83	(65.53)	2.595	+11	..	1.542_5	+1	..	$95._5$	0
84	21.80	13.09	(65.11)	2.573	+ 3	..	1.533_5	+ ½		95	0
85	10.53	24.38	(65.09)	2.649	0	5	1.559	− ½	..	$97._5$	− ½
86	30.87	4.27	(64.86)	....	..	..	1.515	+1		94	0
87	32.82	2.40	64.78	2.509	+ 1	(7)	1.511	+1	(10)	$93._5$	+ ½
87a	35.25	....	(64.75)	2.498	0	(8)	1.507_5	− ½	(10)	94	− ½
88	32.43	3.02	64.55	2.517	− 2	(7)	1.513	0	(10)	94	0
88a	35.50	....	(64.50)	2.500	− 1	9	1.507	0	(10)	$92._5$	+1
89	27.20	8.33	(64.47)	2.546	+ 2	..	1.524	+ ½	..	96	− ½
90	14.15	21.47	64.38	2.638	− 4	8	1.553	− ½	..	97	0
92	(8.22)	28.51	63.27	2.691	− 4	7	1.569_5	0	..	100	− ½
93	....	37.34	62.50	2.746	+ 3	12	1.590_5	0	5	103	0
94	5.11	32.59	62.30	2.719	+ 2	4+	1.580_5	0	12	..	..
95	9.71	28.18	62.11	2.694	0	6	1.570_5	0	6	$100._5$	0
96	38.51	....	61.49	2.515	0	..	1.509_5	0	..	$95._5$	+ ½
96a	28.60	10.04	61.36	2.575	+ 1	3	1.529_5	+ ½	1	97	+1
97	10.42	28.46	61.12	2.702	0	5+	1.571	+ ½	13	$100._5$	+ ½
98	7.44	32.17	(60.39)	2.729	+ 1	10	1.581_5	− ½	12	$102._5$	0
98a	39.66	....	60.34	2.521	0	16	1.511	..	1	..	..
99	16.81	23.04	60.15	2.672	− 2	9	1.560	0	..	100	+ ½
100	19.99	20.00	60.01	2.657	− 7	8	1.553_5	− ½	..	100	0
101	5.01	35.70	59.29	2.761	+ 2	7	1.591	− ½	6	105	− ½
101a	34.08	6.66	59.26	2.562	+ 2	2	1.523_5	+1	3	100	−1
102	9.97	31.14	58.89	2.733	− 1	5	1.580	0	3	$104._5$	− ½
103	26.22	15.00	58.78	2.618	+ 3	6	1.542_5	+ ½	..	100	+ ½
104	17.14	24.24	58.62	2.692	− 6	15	1.563	+ ½	..	102	0
105	28.47	14.31	57.22	2.626	− 2	5	1.542_5	0		101	+ ½
106	15.79	27.07	57.14	2.712	0	..	1.571	0	..	104	0
107	....	42.89	(57.11)	2.835	0	9	1.612	0		$109._5$	− ½
107a	33.91	9.04	57.05	2.588	+ 2	1	1.531	0	4	101	0
107b	13.80	29.40	(56.80)	2.735	− 6	..	....	..		..	..
108	23.06	20.15	56.79	2.665	+ 2	8	1.555	+ ½	17	$102._5$	0
109	44.32	....	(55.68)	2.546	− 5	(5)	1.514	− ½	(10)	$100._5$	½
110	23.50	21.14	(55.36)	2.683	− 4		1.559_5	− ½	10	$105._5$	−1½
111	9.97	34.72	55.31	2.773	0	4	1.590	+ ½	4	$108._5$	−1
112	16.41	28.31	(55.28)	2.733	− 5	7	1.577	−2	10	$106._5$	−1
113	33.87	10.87	(55.26)	2.610	0	..	1.536_5	0	..	102	+1
114	6.13	38.75	55.12	2.808	− 4	6	1.602_5	−1	11	109	− ½
115	4.56	40.42	(55.02)	2.816	+ 2	..	1.606_5	− ½	..	$110._5$	−1
116	41.94	3.33	(54.73)	2.568	− 3	..	1.521_5	− ½	..	$101._5$	+ 1
117	38.32	7.50	54.48	2.587	+ 5	..	1.529	+ ½	..	$101._5$	+2
118	31.33	14.71	(53.96)	2.630	+11	..	1.543_5	+1½	..	$102._5$	+1½
119	21.06	24.97	53.97	2.705	+ 5	6	1.567	+1	13	$104._5$	+1½
120	4.44	42.04	53.52	2.838	− 2	6	1.610_5	− ½	10	111	0
121	5.18	41.50	(53.32)	2.832	− 1	6	1.610	−1	5	$109._5$	+2
122	46.69	....	(53.31)	....	..		1.515	0	(10)	$103._5$	− ½
122a	28.44	18.29	53.27	2.664	+ 3	2	1.552_5	+ ½	0	107	−1½
122b	39.91	7.52	52.57	2.601	0	5	1.531	0	11	105	0
122c	20.80	27.10	(52.10)	2.730	0	..	1.574_5		..	108	− ½
123	31.87	16.08	(52.05)	2.665	− 7	14	1.550_5	−1½	15	106	0
124	10.23	37.98	51.79	2.807	+ 1	3	1.599_5	+ ½	3	$110._5$	+ ½

82. Final melting, 1500°; quenched in H_2O.
93. Difficult to quench, even in mercury.
97. Composition of the compound, $Na_2O \cdot 3CaO \cdot 6SiO_2$.
101. Fined at 1500°; liquidus 1472°; quenched in mercury.
108. Very slightly opalescent when annealed.
114. Liquidus 1493°; melted at 1550°; quenched in H_2O.
119. Only most rapid quenching in thimble crucible gives clear glass which anneals.
122a. Trace of opalescence both before and after annealing.

TABLE XVI. 11—(*Continued*)

					$\times 10^{-3}$			$\times 10^{-3}$	$\times 10^{-4}$		$\times 10^{-4}$
No.	Na_2O	CaO	SiO_2	Observed $d^{20/4}$ annealed	Add to observed d to obtain d of curves	d increased by annealing	Observed n_D annealed	Add to observed n to obtain n of curves	n increased by annealing	Observed $F-C$	Add to observed $(F-C)$ to obtain $(F-C)$ of curves
125	....	48.26	(51.74)	2.898		6	1.629_5	−1	0	$115._5$	−1½
126	10.61	37.63	(51.76)	2.802	+ 4		1.598_5	+ ½	..	111	0
126a	(23.49)	24.95	51.56	2.712	+ 6	6	1.567_5	+1	(12)	..	..
127	18.00	30.65	51.35	2.761	− 4	13	1.584	−2½	15	108	+1
128	39.63	9.16	51.21				1.538	−3		..	..
128a	14.68	34.13	51.19	2.777	+ 4	7	1.589_5	+1	7	$109._5$	+ ½
129	9.88	39.03	(51.09)	2.821	− 3	7	1.603	− ½	8	$111._5$	0
130	17.38	31.65	50.97	2.764	0	9	1.584	0	..	109	+1
131	36.37	12.66	50.97	2.648	− 8	13	1.543_5	−1	13	107	− ½
131a	23.99	25.10	50.91	2.719	+ 2	7	1.568_5	+1	8	109	−1
131b	(37.44)	11.68	50.88	2.641	− 8	(10)	1.540_5	0	(10)	$105._5$	+1
131c	17.52	31.61	50.87	2.761	+ 3	8	....	..	..	..	..
132	49.20	....	(50.80)	2.563	0	(8)	1.517	− ½	(10)	105	0
132a	9.60	39.64	50.76	2.820	+ 2	2	1.604	0	..	112	0
132b	21.40	27.90	50.70	2.741	0	..	1.576	− ½	..	..	..
133	(33.47)	15.98	50.55	2.670	− 8	18	1.550	− ½	(15)	107	0
134	29.77	20.18	50.05	2.696	−16	20	1.560_5	−1½	10	109	−1
134a	34.42	15.54	50.04	2.663	− 2	5	1.549_5	− ½	11	108	− ½
135	26.81	23.57	(49.62)	2.710	+ 5	(9)	1.566	+1	(10)	109	0
136	5.30	45.44	49.26	2.867	+ 3	..	1.620_5	−1	..	$113._5$	+1
136a	50.78	....	49.22								
137	(28.42)	22.46	49.12	2.717	− 7	15	....	..	..	$109._5$	0
137a	30.00	21.00	49.00	2.697	+ 3	8	1.561	+ ½	20	..	..
138	(7.40)	44.30	48.30	2.859	+ 3	..	1.616_5	− ½	..	$114._5$	+ ½
139	....	51.20	(48.80)	2.918	0	8	1.635	0	2	116	+1
140	52.06	....	47.94	2.575	− 2	(8)	1.518	0	(10)	..	..
141	16.98	35.54	(47.48)	2.794	+ 6	..	1.594_5	0	..	$112._5$	+ ½
142	40.76	12.32	(46.92)	2.654	− 1	(8)	1.544_5	− ½	10	$109._5$	+ ½
143	7.98	45.16	46.86	2.863	+ 6	(8)	1.616_5	+2	(5)	115	+1½
144	36.50	17.27	46.23	2.681	+ 2	7	1.555	0	8	110	+1
145	44.77	9.05	46.18	2.630	+ 5	..	1.539	−1	10	111	− ½
146	44.56	10.07	45.37	2.640	+ 4	3	1.540_5	0	2	$111._5$	+ ½
147	9.27	45.38	45.35	2.874	− 1	8	1.619	0	9	118	− ½
148	14.47	40.24	45.29	2.837	0	4	1.606_5	− ½	12	113	−1½
149	4.79	50.06	45.15	2.902	+ 6	(7)	1.630_5	0	(10)	120	−1
150	34.91	20.02	45.07	2.703	+ 2	5	1.562	−1	7	$111._5$	+ ½
150a	55.00	....	45.00	....	..	..	1.519	+ ½	7		
151	22.60	32.50	44.90	2.784	+ 2	13	1.587_5	+ ½	(10)	$114._5$	0
152	....	55.83	44.17	2.953	0	6	1.645_5	0	5	$121._5$	0
153	29.00	27.18	43.82	....			1.578_5	−1½	(7)	$114._5$	− ½
154	20.88	38.16	40.96	....			1.599	0	(5)	119	0
155	26.86	32.24	40.90	2.800	− 7	13	1.587	+1	(7)	..	..
156	38.91	23.43	37.66	2.742	0	(7)	1.574_5	−2	(5)	..	..

125. Slightly milky after 15 min. at 650, but not after 3 hrs. at 565°.

127. Milky after 15 min. at 650°, but not after 3 hrs. at 565°. Very close to composition of compound, $Na_2O \cdot 2CaO \cdot 3SiO_2$.

130. Composition of compound, $Na_2O \cdot 2CaO \cdot 3SiO_2$.

131a. Milky after 6 hrs. at 475°; clear after 4 hrs. at 466°.

133. Quenched in H_2O.

134. Slightly opalescent before and more so after annealing; changes partly due to crystallization.

134a. Practically composition of compound, $2Na_2O \cdot CaO \cdot 3SiO_2$. Necessary to quench in H_2O. Barely trace of opalescence after 4 hrs. at 466, same d after 1½ hrs. at 466°.

135. Clear glass; slightly milky when annealed 12 hrs. at 495°, but n increased 0.020 and d increased 0.031. Microscope shows many minute equant apparently isotropic grains of higher n than glass.

137. Trace opalescence after annealing.

137a. Very milky in 15 hrs. at 475°, $d=2.730$, $n=1.566$; trace of opalescence in 2 hrs. at 475°.

144. Quenched in H_2O.

146. Annealed 2 hrs. at 460°; did not devitrify.

147. Quenched in mercury.

148. Quenched in mercury.

149. Has to be quenched in mercury in foil by dropping; some grains obtained 2 mm. thick.

150. Quenched in mercury.

153. Foil. Drop quench into mercury 2 mm. thick considerably crystallized except at surface no d, but n on edge of prism was obtained. Attempts to anneal caused crystallization.

154. Liquidus 1570°; foil; drop quench in mercury.

155. Liquidus 1570°; foil; drop quench in mercury.

The limiting value of 73.75 per cent for SiO_2 applies only to the lime-free glasses. On addition of lime up to approximately 16 per cent, the values of a, b, and c in the third row are applicable up to 71 per cent SiO_2.

Morey and Merwin[21] measured a much larger range of composition, as is shown in Fig. X. 3. The compositions of the glasses were determined either by analysis or by controlled synthesis. The results are given in Table XVI. 11 and in Figs. XVI. 1, 2, and 3. They could find no justification for expressing the change in index with composition by a series of straight lines. For most of the glasses only the dispersion ($F - C$) was measured, but for some glasses, high in either soda (Na_2O) or lime (CaO), dispersions were measured over a wide range of wavelengths. These are given in Table XVI. 12, together with the dispersions of two optical glasses, for comparison.

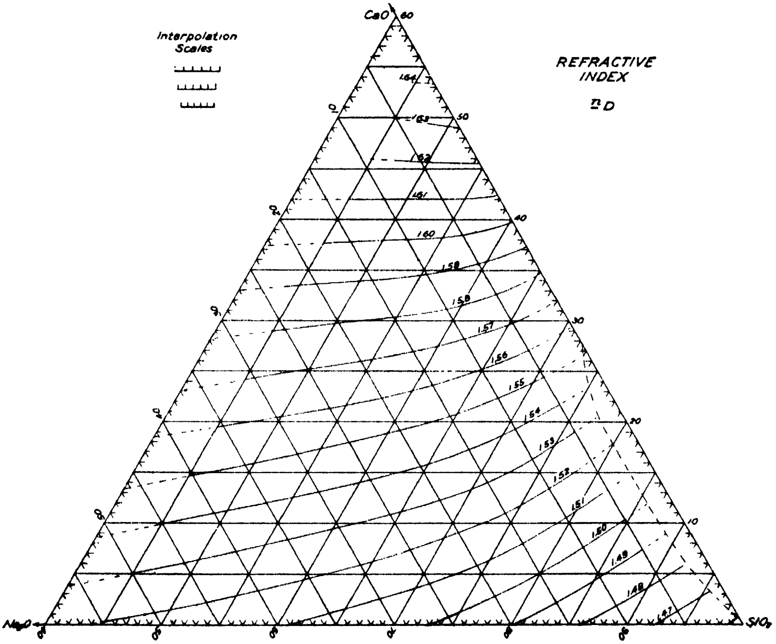

FIGURE XVI. 1.—The Relation Between Refractive Index and Composition in the Ternary System Na_2O-CaO-SiO_2. After Morey and Merwin.

The results of Morey and Merwin gave values of refractive index and of density, measured on the same glasses, and over so wide a range of composition as to make a valuable test of several formulas for specific

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[21] Morey, G. W., and Merwin, H. E., *J. Optical Soc. Am.*, **22**, 632 (1932).

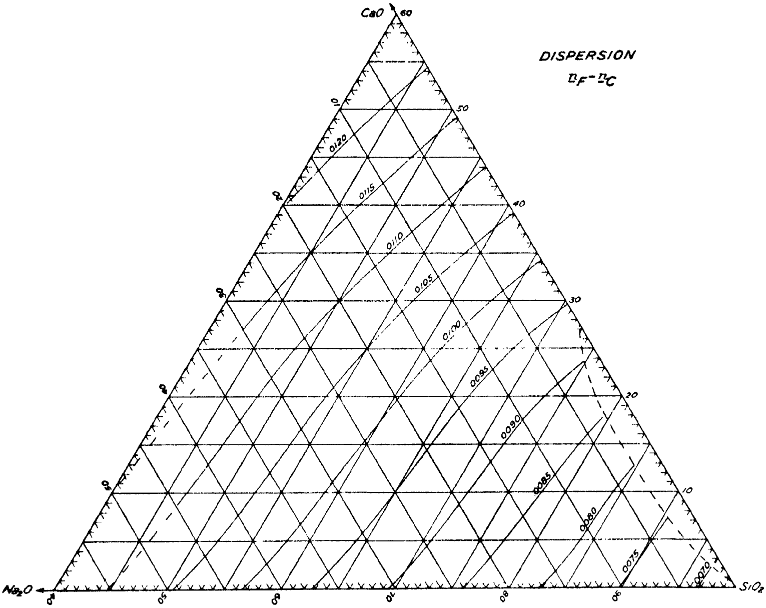

FIGURE XVI. 2.—The Relation between Dispersion and Composition in the System Na_2O-CaO-SiO_2. After Morey and Merwin.

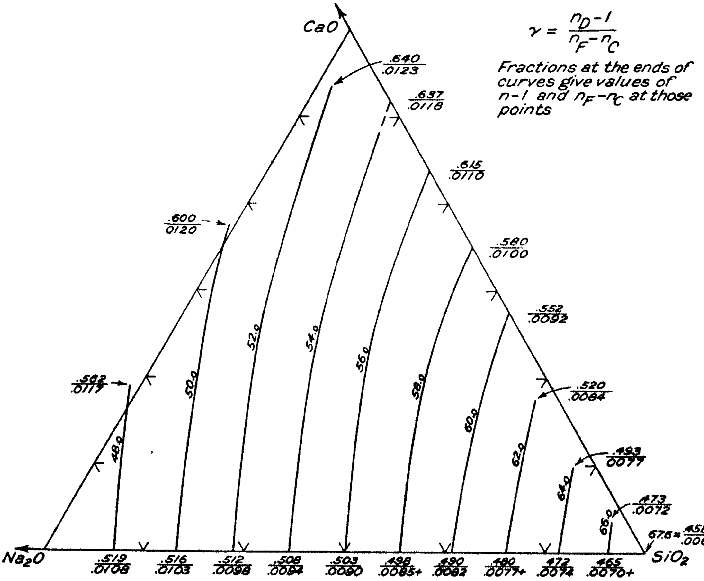

FIGURE XVI. 3.—The Relation between ν-Value and Composition in the System Na_2O-CaO-SiO_2. After Morey and Merwin.

refractivity. Values of specific refractivity were calculated by means of the following formulas: $(n-1)/d$, proposed by Gladstone and Dale[29]; $(n^2-1)/(n^2+2)\cdot 1/d$, proposed by Lorentz[30] and Lorenz[31]; $(n^2-1)/(n+0.4)\cdot 1/d$, proposed by Eykman[32]; and $(\log n)/d$, proposed by Lichtenecker.[33] For each equation the specific refractivity was calculated by assigning to each oxide an arbitrary constant value, and assuming that the specific refractivity is a linear function of the composition. Except for the Lorentz-Lorenz formula, the constant used for silica glass was that calculated from the best values[15] of refractive index and density, namely, $n_D = 1.4585$, $d = 2.203$. The other two constants were adjusted to give a fairly uniform distribution of positive and negative departures. The formulas for the Gladstone-Dale and the Lorentz-Lorenz equations were, respectively:

TABLE XVI. 12—Dispersions of Some Glasses of Unusual Composition

After Morey and Merwin

	$\times 10^{-4}$							
No.	$F-b$	$F-C$	$F-d$	$F-e$	$g-F$	$h-F$	CaO	Na_2O
152	142	*121+*	85	56	67+	*124*	55.83	
		120+		55+	67	*123+*	BaO *ca.* 49%[a]	
139	136+	*117*	81+	53+	64		51.20	
		117				*119+*	BaO *ca.* 45%[b]	
125	135	*115*	79	52+	64	*116*	48.26	
121	129	*110*	77	50+	60+	*111*	41.50	5.18
98	120+	*102+*	72	47	56+	*103*	32.17	7.44
28	104+	*89*	62	41	48+	*88*	20.02	5.73
0	80	*68*	47+	30+	35+	*65*	SiO_2 glass	
3	88+	*75+*	52	34+	40+	*74*		11.83
88a	108+	*93*	64+	43	50+	*94+*		33.50
109	117	*100*	70+	46+	55+	*101+*		44.32
122	119+	*102+*		47+	57	*104+*		46.69
		103				*105+*	PbO *ca*·13%[c]	
132	122+	*105*	73	48+	58+	*107+*		49.20

Wave-lengths in μ: $b = 0.7065$, $C = 0.6563$, $d = 0.5876$, $e = 0.5461$, $F = 0.4861$, $g = 0.4358$, $h = 0.4047$.

[a, b] Barium silicate optical glasses. Small amounts of other oxides do not affect the shape of the dispersion curves in the fourth decimal place.

[c] A flint glass containing about 16 per cent Na_2O. The 13 per cent PbO changes dispersion about like 32 per cent Na_2O.

$$\text{Specific refractivity} = 0.1947N + 0.2268C + 0.2081S \qquad (1)$$
$$\text{Specific refractivity} = 0.1115N + 0.1221C + 0.1237S^{34} \qquad (2)$$

in which N, C, and S represent the percentages by weight of Na_2O, CaO, and SiO_2. Considering the value of the coefficient of the weight percent-

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[29] Gladstone, J. H., and Dale, T. P., *Trans. Roy. Soc. (London)*, **153**, 317, 337 (1863).

[30] Lorentz, H. A., *Ann. Physik Chem.*, **9**, 641 (1880).

[31] Lorenz, L., *Ann. Physik Chem.*, **11**, 70 (1880).

[32] Eykman, J. F., *Rec. trav. chim.*, **14**, 185, 201 (1895).

[33] Lichtenecker, K., *Physik. Z.*, **27**, 115, 833 (1926).

[34] From the best values for silica glass, 0.1239+.

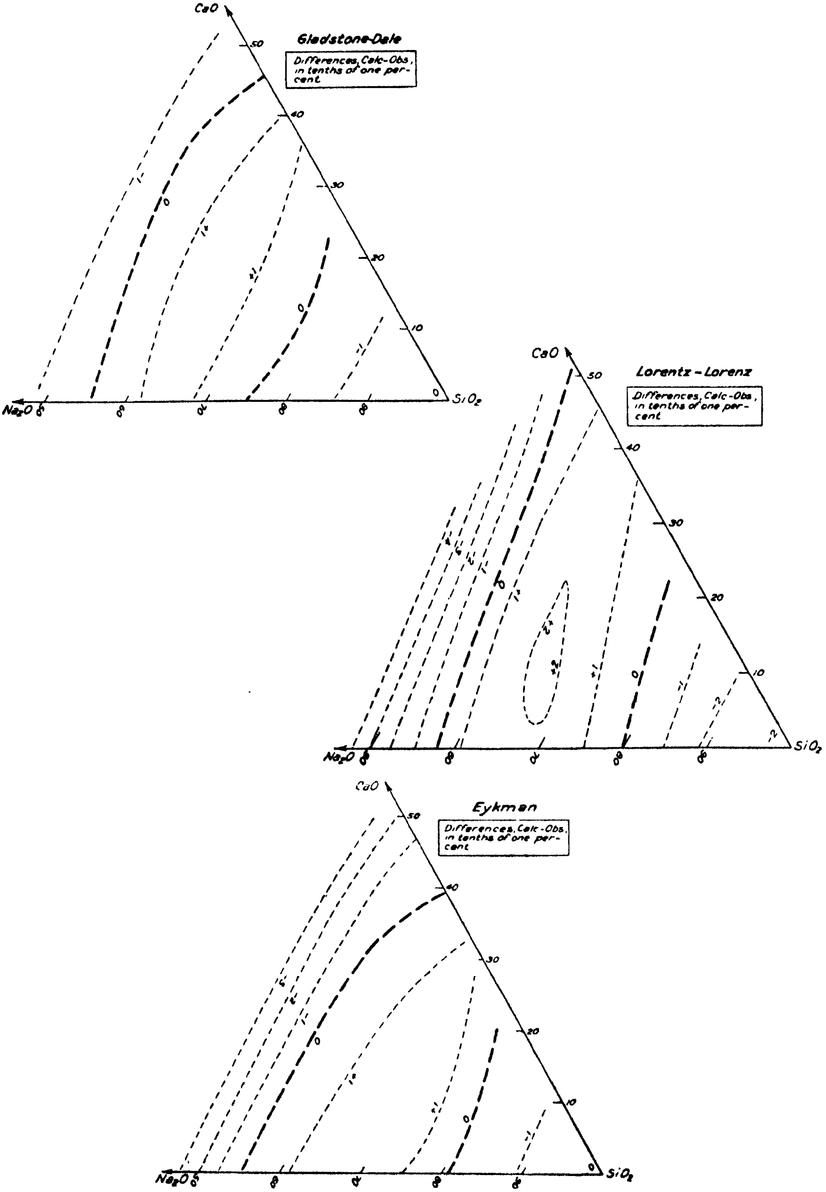

FIGURE XVI. 4.—The Percentage Deviation from an Additive Relationship between Specific Refractivity and Composition in the System Na_2O-CaO-SiO_2. Specific refractivity calculated by means of: (a), the Gladstone-Dale formula, $(n-1)/d$; (b), the Lorentz-Lorenz formula, $(n^2-1)/(n^2+2)\cdot 1/d$; and (c) the Eykman formula, $(n^2-1)/n+0.4)\cdot 1/d$. After Morey and Merwin.

age of SiO_2 as a constant, values of the refractive index and the density of Na_2O and CaO which would satisfy these two expressions were obtained by treating them as simultaneous equations. By this means the values of 1.(586) and 2.(963) were obtained for the refractive index and the density of Na_2O in the glassy state; 1.(777) and 3.(427) for the index and density of CaO in the glassy state. Nothing is known about the properties of crystalline Na_2O, but 1.83 and 3.37 are about the refractive index and density of crystalline CaO.[35]

The constants in the Eykman equation first were calculated from the rough values of the index and density of glassy Na_2O and CaO calculated from the Gladstone-Dale and Lorentz-Lorenz formulas, but the resulting departures were large and positive, and the constants required adjustment. The following formulas were used for calculating specific refractivity from the Eykman and Lichtenecker formulas, respectively:

$$\text{Specific refractivity} = 0.2530N + 0.2807C + 0.2753S \qquad (3)$$

$$\text{Specific refractivity} = 0.6231N + 0.7508C + 0.7440S \qquad (4)$$

The percentage deviations from additivity for the first three formulas are plotted in Fig. XVI. 4, and the fourth formula gave a similar pattern of departures. The maximum contraction on mixing of compositions within the the diagram is about four per cent. While the general pattern of departures is the same for all the formulas tested, the Gladstone-Dale formula gives departures that are little more than one-half as large as the others plotted, and about one-third those of the Lichtenecker formula. For changes due to temperature in organic liquids, the Eykman formula is superior to either the Gladstone-Dale or the Lorentz-Lorenz formula.

Na_2O-ZnO-SiO_2. English, Turner, and Winks[36] measured a series of glasses in which ZnO replaced Na_2O in the glass $Na_2O \cdot 3SiO_2$, with the results given in Table XVI. 10. The irregular results indicate that ZnO, as compared with CaO, has about one-half the effect on refractive index, and about the same effect on dispersion, when the comparison is made on the basis of percentage by weight.

Na_2O-BaO-SiO_2. Peddle[37] studied two series of glasses (Table XVI. 9) in which BaO was added to sodium silicate glasses according to the formula $100SiO_2 + 40$ (or 20) $Na_2O + x$BaO (series 190 and 191); and one series (196) in which SiO_2 was held constant at 70, 65, 60, or 50 per cent by weight and the ratio of BaO to Na_2O was altered. The small meltings were made in clay crucibles, and the contamination introduced by the solvent action of the glass on the crucibles probably explains the irregularities which appear on triangular property-diagrams based on

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[35] *Int. Crit. Tables*, **1**, 143, 165, 344.

[36] English, S., Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **12**, 287 (1928).

[37] Peddle, C. J., *J. Soc. Glass Tech.*, **5**, 201, 228 (1921).

batch compositions. This is especially evident when the BaO content exceeded 25 per cent.

Na_2O-B_2O_3-SiO_2. Two series of glasses in this system were measured by English and Turner,[38] with the results given in Table XVI. 10; the compositions of the glasses are in Table X. 3. In one series, the glasses contained approximately 20 per cent Na_2O, with B_2O_3 replacing SiO_2, and in this series the refractive index increased to a maximum at about 30 per cent B_2O_3. In the second series the Na_2O content was about 10 per cent, and the index fell along this curve to a minimum at about 42 per cent B_2O_3. Dispersions are listed, but they seem high as compared with later measurements by Turner and Winks.[39]

TABLE XVI. 13—Density and Optical Properties of Some Glasses Measured by Larsen

Binary System Albite (Ab) ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$)-Anorthite (An) ($CaO \cdot Al_2O_3 \cdot 2SiO_2$)

Composition	% Ab	% An	n_{Li}	n_D	n_{Tl}	Density
Ab	100	0	1.4864	1.4890	1.4916	2.382
Ab_2An	65.37	34.63	1.5135	1.5166	1.5192	2.483
AbAn	48.55	51.45	1.5278	1.5307	1.5334	2.533
$AbAn_2$	32.05	67.95	1.5420	1.5452	1.5481	2.591
$AbAn_5$	15.87	84.13	1.5563	1.6500	1.5628	2.648
An	0	100	1.5719	1.5755	1.5786	2.700

Binary System $CaO \cdot SiO_2$-$MgO \cdot SiO_2$

% $CaO \cdot SiO_2$	% $MgO \cdot SiO_2$		n_{Li}	n_D	n_{Tl}	Density
100	0		1.6241	1.6280	1.6317	2.904
95	5		1.6223	1.6262	1.6299	2.899
85.26	14.74		1.6185	1.6223	1.6258	2.891
74.00	26.00		1.6135	1.6174	1.6210	2.881
64.00	36.00		1.6084	1.6122	1.6156	2.872
60.00	40.00		1.6067	1.6105	1.6139	2.858
53.64	46.36	(Diopside)	1.6036	1.6071	1.6109	2.854
40.00	60.00		1.5970	1.6007	1.6040	2.834
30.00	70.00		1.5923	1.5960	1.5992	2.821
10.00	90.0		1.5817	1.5853	1.5889	2.789
0	100		1.5767	1.5801	1.5833	2.757

CaO-MgO-SiO_2 glasses

% MgO	% CaO	% SiO_2	n_{Li}	n_D	n_{Tl}	Density
3.50	50.0	46.5	1.6370	1.6410	1.6450	2.953
15.0	40.0	45.0	1.6350	1.6392	1.6428	2.967
25.00	24.8	50.2	1.6183	1.6225	1.6260	2.920

Na_2O-Al_2O_3-SiO_2. The refractive indices of albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) glass measured by Larsen are given in Table XVI. 13. Clarke and Turner [40] measured a few glasses in this system of the general composition $6SiO_2$, $(2 - x)$, xAl_2O_3 (Table XVI. 10).

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[38] English, S., and Turner, W. E. S., *J. Soc. Glass Tech.*, **7**, 155 (1923).

[39] Turner, W. E. S., and Winks, F., *J. Soc. Glass Tech.*, **9**, 389 (1925).

[40] Clarke, J. R., and Turner, W. E. S., *J. Soc. Glass Tech.*, **5**, 119 (1921).

Faick, Young, Hubbard, and Finn[41] measured the refractive index n_D of 44 glasses containing approximately from 1 to 10 per cent alumina, 50 to 78 per cent silica, and 19 to 45 per cent soda, with the results given in Table X. 4. No measurements were made of dispersion. Replacing about 9 per cent of Na_2O by Al_2O_3 lowered both the density and the index; the observed dispersion results, $D - C$ and $F - D$, appear improbable.

TABLE XVI. 14—Optical Properties of Some Unannealed Glasses

After Merwin and Morey

SiO_2	Na_2O	Al_2O_3	n_D	$F - C$ $\times 10^4$	$G-E$	$E-d$	$d-e$	$e-F$	$F-g$	$g-h$
			System Na_2O-Al_2O_3-SiO_2 Partial Dispersions $\times 10^4$							
25.5	22.2	52.3	1.533	100+	17	30	24	46+	55	46+
46.7	18.1	40.2	1.518	92						
41.0	19.1	39.9	1.516	90+	15+	27+	21	42	49+	41
44.7	22.1	33.2	1.512	91						
38.8	28.0	33.2	1.518	96	16+	29	23	44	53	44
55.2	16.0	28.8	1.501	83						
75.0		25.0	1.496	78	13	24	19	35	41	
53.7	23.5	22.8	1.511	92+	16	28	22+	42	51	42
80.0		20.0	1.490	75	13	23	18	34	40	
59.6	30.0	10.4	1.507	92+						
67.5	22.5	10.0	1.499	86+						
47.5	43.2	9.3	1.519	102						
57.9	33.3	8.8	1.509	93						
				System Na_2O-TiO_2-SiO_2						
		TiO_2								
71.8	23.5	4.7	1.520	98	17	30	23	45	56	
68.7	22.1	9.2	1.543	114	19+	34	27	53+	65+	
38.5	31.5	30.0	1.666	213	34	62	50	101+	126+	113
52.6	17.4	30.0	1.676	224	35	65	53	106+	135	120
20.1	29.5	50.4	1.798	342	53	98	80	164	209	191

Merwin and Morey[17] determined refractive indices and partial dispersions for some glasses in this system, with the results given in Table XVI. 14. The glasses were not annealed.

Na_2O-TiO_2-SiO_2. Sheen and Turner[42] studied a series of glasses of the general formula $3SiO_2$, $(2 - x)$ Na_2O, $xTiO_2$. The optical results are given in Table XVI. 10; the compositions of the glasses, as determined by analysis, in Table X. 3. The run of the dispersions (particularly of a glass near 75 per cent SiO_2, 25 per cent Na_2O, for which data are numerous) indicates some large error in the measurements, which were made on a Pulfrich refractometer. The heat treatment which the glasses had received was not mentioned, but in the same paper a study was made of the annealing temperature, and presumably these glasses had

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[41] Faick, C. A., Young, J. C., Hubbard, D., and Finn, A. N., *J. Research Natl. Bur. Standards*, **14**, 133 (1935); RP 762.

[42] Sheen, A. R., and Turner, W. E. S., *J. Soc. Glass Tech.*, **8**, 187 (1924).

been annealed in accordance with that study. Titania, replacing soda in the trisilicate glasses, increased the refractive index more than lime; a glass containing 9.80 per cent TiO_2 had an index of 1.539, and one of similar composition, but containing 9.36 CaO in place of titania, had an index of 1.515.

Merwin and Morey[17] determined refractive indices and partial dispersions for some glasses in this system, with the results given in Table XVI. 14. The glasses were not annealed.

Na_2O-PbO-SiO_2. Peddle[43] measured the refractive indices for the *C*, *D*, and *F* lines of two series of glasses of the general formula $100SiO_2 + 40$ (or 20) $Na_2O + x$ moles PbO, and one series (187) in which SiO_2 was held constant at 70, 65, 60, 50, 40, or 30 per cent by weight, and the ratio of Na_2O to PbO was altered. The results are given in Table XVI. 9. Both silica and alumina, probably more than two per cent, were introduced into the glasses of higher refractive index by attack on the clay crucible during melting, which probably accounts for irregularities of more than 0.01 in the value of n_D, evident when all measurements are plotted on a triangular diagram based on batch composition. Optical properties of some glasses high in PbO, measured by Merwin and Andersen, are included in Table XVI. 7.

TABLE XVI. 15—Properties of Some Glasses Containing Bismuth Oxide

After Riegel and Sharp

No.	Na_2O	Bi_2O_3	Density	n_D	$n_F - n_C$	γ
35B1	24.30	12.71	2.725	1.535		
35B2	23.78	12.40	2.7166	1.5352	0.01119	47.8
40B1	22.73	20.67	2.941	1.565		
40B2	21.87	22.00	2.9561	1.5697	0.01333	42.7
45B1	20.83	29.52	3.171	1.600		
45B2	19.18	29.66	3.1801	1.5948	0.01546	38.5
50B1	18.23	34.34	3.333	1.624		
50B2	14.99	34.51	3.3699	1.6109	0.01673	36.5
60B2	14.24	44.92	3.7629	1.6668	0.02144	31.5
60B1	14.48	45.75	3.73	1.670		
70B1	13.55	52.87	4.110	1.712		

Na_2O-Bi_2O_3-SiO_2. Riegel and Sharp[44] made a series of glasses of the general formula $100SiO_2$, $40Na_2O$, xBi_2O_3, a composition range chosen to make the glasses comparable with a series of glasses containing PbO made by Peddle (Table XVI. 9, series 180). Measurements were made with Abbé and Pulfrich refractometers, and with a spectrometer. The results are given in Table XVI. 15. Meltings in the B1 series were made in 100-gram lots, and in the B2 series in 400-gram lots. They were heated

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[43] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 299, 330 (1920).

[44] Riegel, E. R., and Sharp, D. E., *J. Am. Ceram. Soc.*, **17**, 88 (1934).

two to three hours at 1300°. Compared on the basis of equal percentages by weight, the glasses containing bismuth oxide had a higher index than those containing lead oxide.

Na_2O-Fe_2O_3-SiO_2. In their study of the phase equilibrium relationships in the ternary system Na_2SiO_3-Fe_2O_3-SiO_2, a part of the system

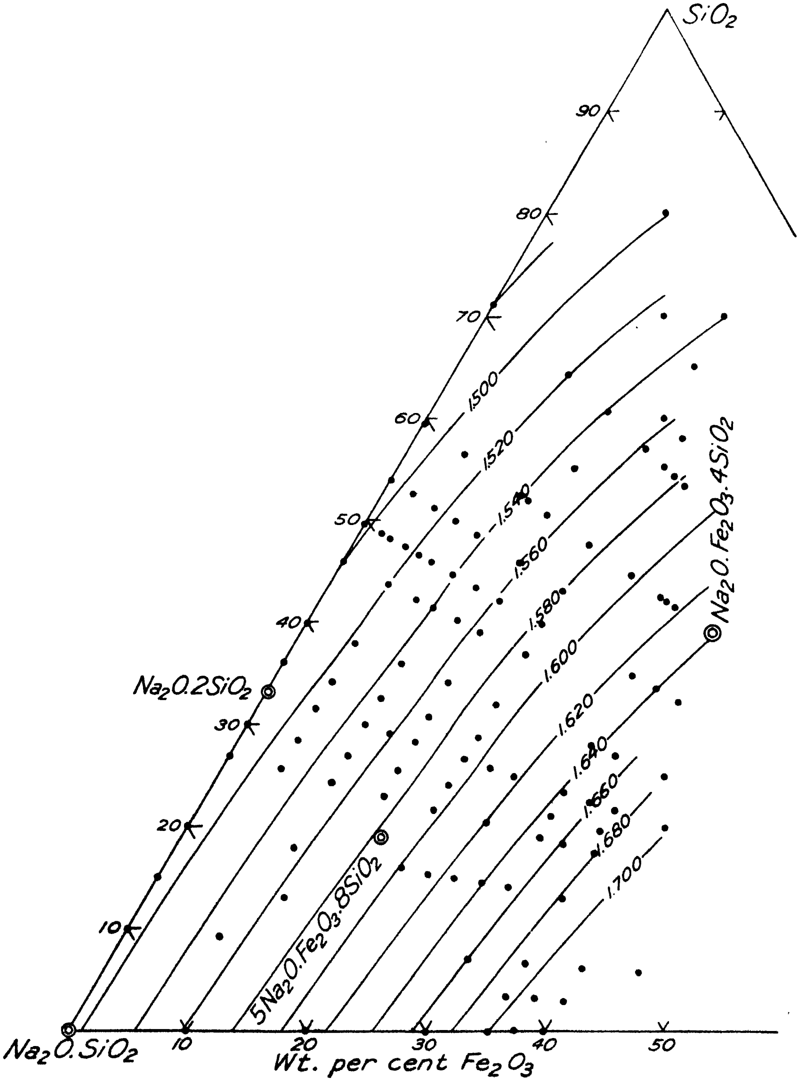

FIGURE XVI. 5.—The Relation between Refractive Index and Composition in the System Na_2O-Fe_2O_3-SiO_2. After Bowen, Schairer and Willems.

TABLE XVI. 16—Refractive Indices of Glasses in the System Na_2O-Fe_2O_3-SiO_2

After Bowen, Schairer and Willems

Composition in weight per cent Na_2O	Fe_2O_3	SiO_2	Refractive index $n \pm .003$
22.78	2.50	74.72	1.504
19.49	5.00	75.51	1.512
18.46	10.00	71.54	1.533
13.21	10.00[a]	76.79	1.522
15.24	15.00	69.76	1.547
12.48	15.00	72.52	1.543
11.74	20.00	68.26	1.563
10.16	20.00	69.84	1.555
20.06	6.00	69.94	1.523
23.68	7.50	68.82	1.529
21.61	7.50	70.89	1.527
25.23	8.00	66.77	1.532
27.43	10.00	62.57	1.544
24.68	10.00	65.32	1.541
23.04	10.00[b]	66.96	1.541
21.03	10.00	68.97	1.538
24.00	12.50	63.50	1.552
22.40	12.50	65.10	1.552
17.95	12.50	69.55	1.544
16.51	14.00	69.49	1.545
27.63	15.00	57.37	1.569
25.90	15.00	59.10	1.568
23.31	15.00	61.69	1.564
21.76	15.00	63.24	1.563
19.86	15.00	65.14	1.559
17.44	15.00	67.56	1.553
28.25	17.00	54.75	1.579
27.23	20.00	52.77	1.593
26.00	20.00	54.00	1.591
24.38	20.00	55.62	1.591
21.94	20.00	58.06	1.587
20.48	20.00	59.52	1.585
18.69	20.00	61.31	1.581
16.41	20.00	63.59	1.575
11.74	20.00	68.26	1.563
26.38	22.50	51.12	1.606
11.38	22.50	66.12	1.572
26.67	25.00	48.33	1.619
25.53	25.00	49.47	1.617
15.38	25.00	59.62	1.595
24.89	30.00	45.11	1.646
23.81	30.00	46.19	1.643
21.33	30.00	48.67	1.636
17.92	30.00	52.08	1.629
20.57	32.50	46.93	1.651
7.62	20.00	72.38	1.548
9.90	22.50	67.60	1.566
11.19	23.75	65.06	1.576
11.01	25.00	63.99	1.584
14.67	28.50[c]	56.83	1.611
14.51	29.25	56.24	1.614
28.44	30.00	41.56	1.654
25.95	30.00[d]	44.05	1.647
14.36	30.00	55.64	1.617
24.18	32.00	43.82	1.659
25.03	32.50	42.47	1.661
22.96	32.50	44.54	1.658

Composition in weight per cent Na_2O	Fe_2O_3	SiO_2	Refractive index $n \pm .003$
20.57	32.50	46.93	1.651
17.28	32.50	50.22	1.641
29.71	35.00	35.29	1.687
26.41	35.00	38.59	1.682
24.10	35.00	40.90	1.678
23.11	35.00	41.89	1.677
22.12	35.00	42.88	1.672
16.64	35.00[e]	48.36	1.653
19.05	37.50	43.45	1.679
27.43	40.00	32.57	1.719
20.43	40.00	39.57	1.698
25.28	1.25	73.47	1.503
22.20	5.00	72.80	1.516
18.10	11.75	70.15	1.540
17.95	12.50	69.55	1.544
16.51	14.00	69.49	1.545
25.09	2.00	72.91	1.507
24.83	3.00	72.17	1.510
24.45	4.50	71.05	1.517
35.22	5.00	59.78	1.530
33.78	5.00	61.22	1.528
32.32	5.00	62.68	1.526
30.88	5.00	64.12	1.525
28.95	5.00	66.05	1.523
26.06	5.00	68.94	1.519
32.00	10.00	58.00	1.549
30.62	10.00	59.38	1.548
29.26	10.00	60.74	1.546
27.43	10.00	62.57	1.544
34.32	10.00	55.68	1.553
33.37	10.00[f]	56.63	1.552
32.00	10.00	58.00	1.549
29.77	12.50	57.73	1.558
31.52	15.00	53.48	1.574
30.22	15.00	54.78	1.572
28.92	15.00	56.08	1.569
32.62	16.81	50.57	1.583
29.67	20.00	50.33	1.597
28.44	20.00	51.56	1.595
31.49	22.50	46.01	1.613
30.48	25.00	44.52	1.626
27.81	25.00	47.19	1.621
26.67	25.00	48.33	1.619
29.46	27.50	43.04	1.639
31.74	37.50	30.76	1.716
30.48	40.00	29.52	1.732
28.95	40.00	31.05	1.724
36.23	5.00	58.77	1.529
42.06	8.00	49.94	1.548
45.71	10.00	44.29	1.562
36.57	10.00	53.43	1.554
38.21	11.50	50.29	1.562
40.63	20.00	37.37	1.612
32.51	20.00	47.49	1.602
35.55	30.00	34.45	1.667
32.00	30.00	38.00	1.657
33.01	35.00	31.99	1.701
31.36	35.00	33.64	1.693

[a] Contained 0.34% FeO at 1,180°.

[d] Contained 0.40% FeO at 838°.

TABLE XVI. 17—Optical Properties and Densities of Glasses in the System K_2O-CaO-SiO_2

After Merwin and Morey

No.	K_2O	CaO	SiO_2	Density (annealed) $d^{20/4}$	Density increase on annealing × 10^3	Refractive Index (annealed) n_D	Increase in n_D on annealing × 10^3	$F - C$ × 10^4
1	5		95			1.463		69+
2	10		90			1.468		73
3	5.1	9.8	85.1	2.360	4	1.495	0.5	78+
4	17.5		82.5	2.322		1.482	0.5	76+
5	15.0	5.0	80.0	2.37_1*		1.49_3		78
6	11.6	9.1	79.3	2.412		1.503	0.5	81
7	13.7	10.5	75.8			1.508	0.5	
8	19.8	5.0	75.2	2.412		1.500+		82
9	24.8		75.2	2.375	5	1.491+	2.	81
10	26.3		73.7	2.389		1.493		81
11	10.5	16.9	72.6	2.501	3	1.526	0.5	88+
12	17.3	10.2	72.5	2.448	8	1.510+	1.	84
13	12.6	15.0	72.4	2.492	8	1.521+		87
14	5.4	22.4	72.2	2.546	5	1.510	1.5	89+
15	8.4	19.8	71.8	2.528	(5)			
16	27.3	1.0	71.7	2.40_5	9	1.495	(0.5)	83
17	28.3		71.7	2.399		1.495		81
18	29.1		70.9	2.396	8	1.495		81+
19	18.3	11.0	70.7	2.473	7	1.516		86+
20	20.4	9.9	69.7	2.473	(10)			
21	22.4	8.1	69.5	2.461		1.511+	(1)	85
22	24.3	7.6	68.1	2.470		1.512+		85
23	32.1		67.9	2.423	(9)	1.498		83
24	34.1		65.9	2.42_6		1.502		84+
25	3.9	30.4	65.7	2.659	4	1.567	1.	97+
26	34.6		65.4	2.426		1.501		
27	10.5	24.4	65.1	2.593	3	1.551	1	95
28	12.7	22.6	64.7	2.584	4	1.547	1	92
29	16.6	19.8	63.6	2.569	4	1.541+	1	92
30	28.3	8.4	63.3	2.498		1.518+		88
31		37.4	62.6	2.746	12	1.590+	0.5	103
32	22.1	15.4	62.5	2.544		1.533	0.5	90
33	32.6	4.9	62.5	2.481		1.513		87
34	30.7	7.7	61.6	2.502	11		2	88+
35	32.2	7.2	60.6	2.500		1.518+	2.5	88
36	25.4	14.1	60.5	2.546	5	1.532	2	92+
37	24.7	15.4	59.9	2.554	7	1.534	1	92
38	8.6	31.7	59.7	2.189	3	1.574	0.5	99+
39	31.4	9.3	59.3	2.519		1.523		91+
40	41.0		59.0			1.506	(1)	87
41	41.1		58.9			1.506	(1.5)	86
42	34.3	7.2	58.5	2.509		1.519+		90
43	27.7	14.6	57.7	2.560	12	1.533+	1.5	93+
44	20.0	22.3	57.7	2.613	3	1.511	0.5	96
45		42.9	57.1	2.835	9	1.612		109+
46	38.3	4.7	56.9	2.505	12	1.518		90
47	43.3		56.7	2.46_7		1.508+		89+
48	15.2	29.7	55.1	2.683	5	1.570	1	100+
49	5.3	39.9	54.8	2.783	4	1.597+	0.5	107
50	28.3	17.0	54.7	2.596	9	1.544	(0.5)	96
51		48.3	51.7	2.898	6	1.629+	0	115+

* Subscript numbers are less precise.

TABLE XVI. 17—(*Continued*)

No.	K_2O	CaO	SiO_2	Density (annealed) d^{20°	Density increase on annealing × 10^3	Refractive Index (annealed) n_D	Increase in n_D on annealing × 10^3	$F - C$ × 10^4
52	24.6	24.9	50.5			1.585	(1)	101
53	34.0	15.6	50.4	2.606		1.547		99
54	9.6	40.6	49.8	2.793		1.601	0	109
55	30.6	19.7	49.7	2.63_5	8	1.555+	1.5	101
56		51.2	48.8	2.918	8	1.635	0	116
57	25.1	26.5	48.4	2.686	9	1.569	1.5	105
58	46.0	5.8	48.2	2.542		1.527+	(1)	96+
59	27.7	24.2	48.1	2.665		1.565	(1)	103
60	24.3	29.0	46.7	2.701		1.575		106
61	34.5	20.7	44.8	2.658		1.560+		103
62		55.8	44.2	2.953	6	1.645+	0.5	121+
63	32.8	23.5	43.7	2.672	9	1.564	(0.5)	104
64	17.9	39.6	42.5			1.603	(0.5)	
65	16.5	41.4	42.1	2.80_0	2	1.60_8		114
66	47.9	10.6	41.5			1.544	(1)	

Na_2O-Fe_2O_3-SiO_2, Bowen, Schairer, and Willems[45] measured microscopically by the immersion method the refractive indices of the glasses, with the results shown in Fig. XVI. 5, and given in Table XVI. 16. Some FeO was always present; the amount in six of the glasses was determined and is indicated in a footnote in the table.

K_2O-BeO-SiO_2. Lai and Silverman[46] measured the refractive index, n_D, for some glasses in this system, with the results given in Table X. 6. Batch compositions were given of the small meltings, which were made in clay crucibles.

K_2O-CaO-SiO_2. Measurements in this system by Peddle[47] are included in Table XVI. 9. The glasses were not analyzed and probably contained significant amounts of impurities derived by solution of the clay melting-pot. Two series (167 and 168) represented addition of CaO to the glasses $100SiO_2 + 40$ (or 20) K_2O; another series (175) was based on the formula $100SiO_2 + 13.16K_2O + x$CaO, which gave percentages by weight of K_2O equivalent to those of Na_2O in the series $100SiO_2 + 20Na_2O + x$CaO; and still another (171) was made in which the SiO_2 was held constant at 70, 65, or 60 per cent while the proportions of K_2O and CaO were altered. These potash-lime-silica glasses had a lower refractive index and a lower total dispersion than soda-lime-silica glasses with equal percentages by weight.

A more extensive series of measurements in this system is that of Merwin and Morey,[17] given in Table XVI. 17. The glasses measured were some of those used in a previous study[48] of the phase equilibrium

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[45] Bowen, N. L., Schairer, J. F., and Willems, H. W. V., *Am. J. Sci.*, **20**, 405 (1930).

[46] Lai, C. F., and Silverman, A, *J. Am. Ceram. Soc.*, **13**, 393 (1930).

[47] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 46, 71 (1920).

[48] Morey, G. W., Kracek, F. C., and Bowen, N. L., *J. Soc. Glass Tech.*, **14**, 149 (1930); **15**, 57 (1931). See Fig. II. 10.

relations in this system; the methods used in measuring the optical properties and the density were those used for glasses in the system Na_2O-CaO-SiO_2 (p. 387). The properties of the annealed glasses are given in the table, together with the changes of many of them in density and refractive index produced by annealing at about 500°.

TABLE XVI. 18—Refractive Index of Glasses in the System K_2O-Fe_2O_3-SiO_2

After Faust

Series No.	Composition by Synthesis			Index of Refraction	Rough Estimate of Color
	% K_2O	% F_2O_3	% SiO_2		
400	28.17		71.83	1.494	Clear
404	27.04	4.00	68.96	1.510	Very light brown
418	23.10	18.00	58.90	1.564	Brown
423	21.69	23.00	55.31	1.585	Deep brown
425	21.13	25.00	53.87	1.599	Deep brown
432	19.06	32.32	48.62	1.621	Very dark brown—almost black
500	23.88		76.12	1.489	Clear
503	23.16	3.00	73.84	1.502	Light yellow
506	22.45	6.00	71.55	1.515	Dark yellow
510	21.49	10.00	68.51	1.528	Yellow brown
520	19.10	20.00	60.90	1.566	Brown
523	18.39	23.00	58.61	1.578	Brown
600	20.72		79.28	1.486	Clear
602	20.31	2.00	77.69	1.493	Light yellow
606	19.48	6.00	74.52	1.509	Yellow
607.5	19.17	7.50	73.33	1.513	Yellow
610	18.65	10.00	71.35	1.524	Light brown
615	17.61	15.00	67.39	1.543	Light brown
617.5	17.09	17.50	65.41	1.552	Light brown
620	16.58	20.00	63.42	1.562	Brown
620.5	16.47	20.50	63.03	1.562	Brown
621	16.37	21.00	62.63	1.563	Brawn
623	15.95	23.00	61.05	1.571	Brown
625	15.54	25.00	59.46	1.579	Very dark brown
626	15.33	26.00	58.67	1.582	Very dark brown—almost black
700	18.31		81.69	1.483	Clear
712	16.11	12.00	71.89	1.528	Light brown
715	15.56	15.00	69.44	1.541	Light brown
718	15.01	18.00	66.99	1.551	Brown
720	14.64	20.00	65.36	1.559	Brown

K_2O-BaO-SiO_2. The results of Peddle[49] on this system are included in Table XVI. 9. Series 192 and 193 were of the general formula $100SiO_2 + 40$ (or 20) $BaO + xBaO$. The SiO_2 content was held constant in series 201 at 70, 65, 60, or 50 per cent by weight, and the ratio of BaO to K_2O was altered. The batch compositions given represent only roughly the actual compositions of some of the glasses. Increase in the BaO content increased the index, and the potash glasses had a lower

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[49] Peddle, C. J., *J. Soc. Glass Tech.*, 5, 212, 228 (1921).

refractive index than the corresponding soda glasses. As the BaO was increased, with consequent decrease in alkali content, both the ν-value and the dispersion decreased, and the effect was greater for the potash glasses than for the soda glasses. When the ratio $K_2O:SiO_2$ was constant, addition of BaO increased the refractive index and the dispersion. When compared with corresponding compositions in the soda series, the potash glasses here had lower refractive indices, by about 0.006, and lower dispersions ($F - C$), by about 0.003, and slightly higher ν-values.

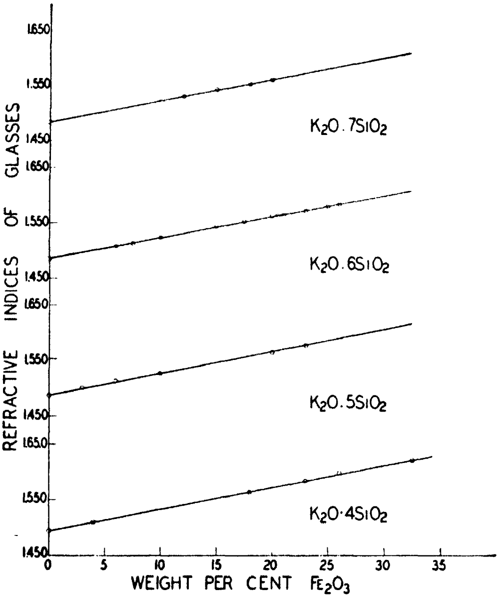

FIGURE XVI. 6.—Change in Refractive Index with Addition of Fe_2O_3 in some Glasses of the Original Composition shown. After Faust.

K_2O-PbO-SiO_2. Peddle measured two series of glasses (182 and 183) of the general formula $100SiO_2 + 40$ (or 20) $K_2O + x$PbO; and one series (187) in which the SiO_2 content was held constant at 70, 65, or 60 weight per cent and the ratio of K_2O to PbO was altered. The results are given in Table XVI. 9. Batch compositions only are given, but corrosion of the clay crucibles added silica and alumina to the glasses to such an extent that triangular plots of property against batch composition show large irregularities, amounting to 0.015 for n_D and 0.0016 for $F - C$. Even larger differences are found when these glasses are compared with glasses of known composition. These potash glasses have lower refractive indices and dispersions than soda glass of corresponding batch compositions in weight per cent. This is true to about

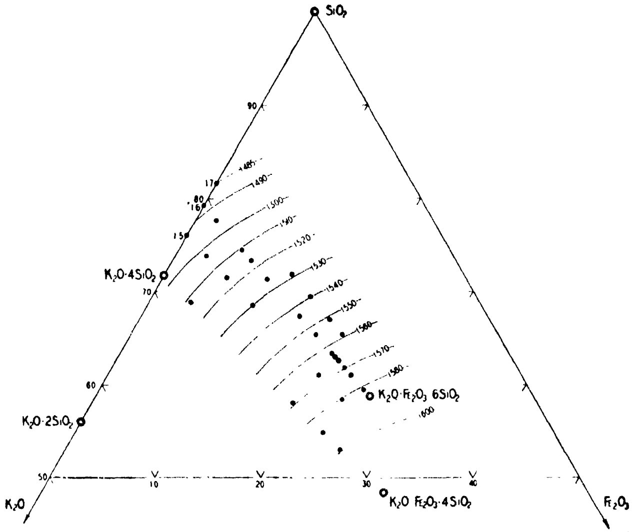

FIGURE XVI. 7.—The Relation between Refractive Index and Composition in the System K_2O-Fe_2O_3-SiO_2. After Faust.

the same extent for pure potash-silica and soda-silica glasses. Table XVI. 7 gives some measurements made by Merwin and Andersen on glasses in this system.

K_2O-Fe_2O_3-SiO_2. Faust[50] measured the refractive index of glasses in this system, with the results shown in Table XVI. 18 and in Figs. XVI. 6 and 7.

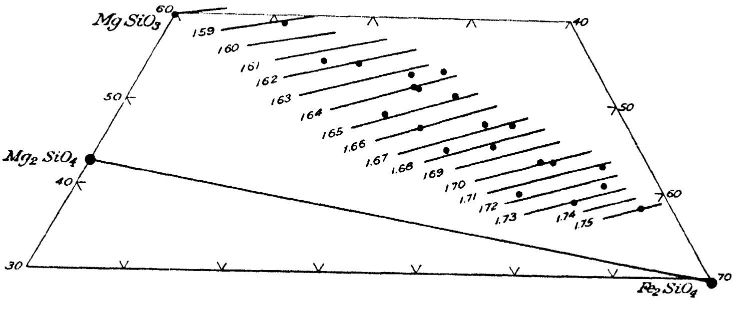

FIGURE XVI. 8.—The Relation between Refractive Index and Composition in the System MgO-FeO-SiO_2. After Bowen and Schairer.

MgO-CaO-SiO_2. Larsen[22] measured the refractive index of glasses on the metasilicate join, and of three other glasses, for lithium

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[50] Faust, G. T., Private communication; to be published in *J. Am. Ceram. Soc.*

($\lambda = 670.8\,\mathrm{m}\mu$), sodium and thallium ($\lambda = 535.0\,\mathrm{m}\mu$) light. Measurements were made on prisms by the minimum deviation method, with a probable error of ± 0.0003. Compositions were correct to 0.3 per cent; the thermal history of the glasses was not given. The results are in Table XVI. 13.

MgO-FeO-SiO_2. The compositions which could be obtained as glass by Bowen and Schairer [51] in their study of the phase equilibrium relationships in this system are shown in Fig. XVI. 8. The glasses were melted in electric furnaces, using iron crucibles in a current of nitrogen, but some Fe_2O_3 was always formed, the amount depending on the temperature and the composition of the melt. Table XVI. 19 gives the compositions of the melts at the liquidus temperature, and the refractive indices of the glasses, determined by the immersion method on quickly cooled samples.

TABLE XVI. 19—Refractive Indices of Glasses in the System MgO-FeO-SiO_2

After Bowen and Schairer

Composition of liquid at liquidus temperature				Refractive index	Composition of liquid at liquidus temperature				Refractive index
FeO	Fe_2O_3	MgO	SiO_2	$n \pm .003$	FeO	Fe_2O_3	MgO	SiO_2	$n \pm .003$
17.53	0.26	27.63	54.58	1.616	44.30	1.25	14.85	39.60	1.716
21.15	0.28	24.21	54.36	1.621	37.30	0.61	14.55	47.54	1.668
32.38	0.48	16.03	51.11	1.648	30.66	0.79	21.55	47.00	1.661
57.73	1.38	3.07	37.82	1.750	26.51	0.58	24.30	48.61	1.648
52.59	0.95	5.66	41.80	1.725	26.44	0.59	19.45	53.52	1.633
50.25	1.13	9.72	38.90	1.730	28.35	0.69	19.30	51.66	1.642
46.18	0.93	9.40	43.29	1.702	40.05	0.63	11.87	47.45	1.672
44.80	1.11	10.80	43.29	1.700	51.36	0.89	4.78	42.97	1.713
39.05	1.04	14.98	44.93	1.687	29.83	0.59	15.91	53.67	1.638

CaO-SrO-SiO_2 and CaO-BaO-SiO_2. Eskola [23] measured glasses in these two systems along the metasilicate join, *i. e.*, for the binary systems $CaO \cdot SiO_2$-$SrO \cdot SiO_2$ and $CaO \cdot SiO_2$-$BaO \cdot SiO_2$, with the results given in Table XVI. 8. He used Merwin's improved immersion method, and determined refractive indices for the *F*, *D*, and *C* lines, and for thallium light ($\lambda = 535\,\mathrm{m}\mu$).

CaO-FeO-SiO_2. Bowen, Schairer, and Posnjak [52] studied the phase equilibrium relations in this system and measured the refractive indices of all mixtures that could be obtained as glass, with the results given in Table XVI. 20. The immersion method was used, with a probable error of ± 0.003, on quickly cooled samples. The mixtures were melted in iron crucibles in an atmosphere of nitrogen. All contained small amounts of ferric iron, the quantity of which is given in the table. Fig. XVI. 9

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[51] Bowen, N. L., and Schairer, J. F., *Am. J. Sci.*, **29**, 151 (1935).

[52] Bowen, N. L., Schairer, J. F., and Posnjak, E., *Am. J. Sci.*, **26**, 193 (1933).

shows the change in refractive index with composition, all the iron being calculated as ferrous oxide.

Na_2O-K_2O-CaO-SiO_2. Glasses in this system were measured by Peddle,[53] with the results given in Table XVI. 9. Batches for series 169 were based on the formula $100SiO_2 + 20Na_2O + 20K_2O + x CaO$; for 170, on the formula $100SiO_2 + 10Na_2O + 10K_2O + x CaO$. In series 171 SiO_2 was held constant, Na_2O and K_2O were added in equal amounts, and the ratio of total alkali to CaO was altered. As to final compositions these glasses should be compared with similarly planned glasses in the ternary systems containing one alkali. The refractive index and dispersion of a glass containing half of its molecular alkali as Na_2O and half as K_2O were between those of glasses containing only Na_2O or K_2O, and tended to be nearer the glass containing only Na_2O.

TABLE XVI. 20—Refractive Indices of Glasses in the System CaO-FeO-SiO_2

After Bowen, Schairer and Posnjak

Composition of liquid at liquidus temperature				Refractive index	Composition of liquid at liquidus temperature				Refractive index
FeO	Fe_2O_3	CaO	SiO_2	$n \pm .003$	FeO	Fe_2O_3	CaO	SiO_2	$n \pm .003$
6.50	0.30	42.68	50.52	1.636	28.74	2.19	32.56	36.51	1.725
8.62	0.58	40.35	50.45	1.639	31.12	1.74	29.62	37.52	1.725
11.94	0.64	37.59	49.83	1.648	32.14	1.88	29.56	36.42	1.735
14.44	0.46	35.27	49.83	1.650	27.61	1.26	28.70	42.43	1.699
17.78	0.62	32.47	49.13	1.656	29.09	1.00	25.24	44.67	1.690
19.71	0.75	30.44	49.10	1.657	34.27	1.31	24.02	40.40	1.717
25.32	0.96	25.11	48.61	1.669	31.68	1.56	28.90	37.86	1.725
28.96	0.74	22.31	47.99	1.675	32.23	2.03	29.88	35.86	1.735
31.73	1.16	19.25	47.86	1.678	33.69	1.63	28.86	35.82	1.734
34.15	0.84	17.01	48.00	1.680	38.23	1.61	23.67	36.49	1.740
36.71	1.18	14.55	47.56	1.685	41.55	0.79	15.58	42.08	1.720
41.76	1.15	9.77	47.32	1.691	41.27	1.19	19.26	38.28	1.737
15.00	0.63	27.79	56.68	1.622	45.04	1.33	13.37	40.26	1.734
19.73	0.76	24.85	54.66	1.632	43.95	1.05	12.00	43.00	1.715
27.61	0.74	20.99	50.66	1.668	5.21	0.50	51.61	42.68	1.662
45.22	1.01	10.36	43.41	1.715	16.43	1.50	43.51	38.56	1.688
52.04	0.90	5.51	41.55	1.735	20.86	1.36	40.88	36.90	1.712
5.40	0.35	34.72	59.53	1.602	33.69	1.63	28.86	35.82	1.734
10.75	0.44	34.54	54.27	1.628	45.97	1.92	18.04	34.07	1.77
14.92	1.14	40.49	43.45	1.673	48.09	1.52	14.41	35.98	1.76
17.05	1.69	42.10	39.16	1.688	54.42	1.73	9.72	34.13	1.79
20.84	0.99	33.51	44.06	1.681	48.73	1.49	11.19	38.59	1.745
22.55	1.50	36.67	39.28	1.706	52.96	1.09	9.01	36.94	1.765
23.60	2.11	37.15	37.14	1.714	53.30	0.98	5.96	39.76	1.745
23.83	1.09	35.04	40.04	1.708					

Na_2O-K_2O-PbO-SiO_2. Peddle[54] made three series of glasses in this system, with the results included in Table XVI. 9. Batches for series 184 were based on the formula $100SiO_2 + 20Na_2O + 20K_2O + x PbO$; for series 185 on $100SiO_2 + 10Na_2O + 10K_2O + x PbO$. In series 168,

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[53] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 59, 71 (1920).

[54] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 320, 330 (1920).

Na_2O and K_2O were each held constant at 10 per cent and the ratio of SiO_2 to PbO was altered. For final compositions and results the phases should be compared with the corresponding series containing only one alkali. The mixed glasses were intermediate both in index and dispersion between the corresponding glasses containing only Na_2O or K_2O. Some glasses in this system, measured by Merwin and Andersen, are included in Table XVI. 7.

Na_2O-K_2O-BaO-SiO_2. Glasses in this system were measured by Peddle [55] and are included in Table XVI. 9. For batches in series 194 the compositions were based on the formula $100SiO_2 + 20Na_2O + 20K_2O + x$BaO; in 195, on $100SiO_2 + 10Na_2O + 10K_2O + x$BaO. In series 202 mixed glasses containing the same percentages by weight of Na_2O and K_2O, with SiO_2 held constant at 70, 65, 60, or 50 per cent, were made by altering the ratio of total alkali to BaO. These glasses should be compared as to final composition with the corresponding ones containing only one alkali. The mixed glasses were intermediate in properties between the corresponding glasses containing only Na_2O or K_2O.

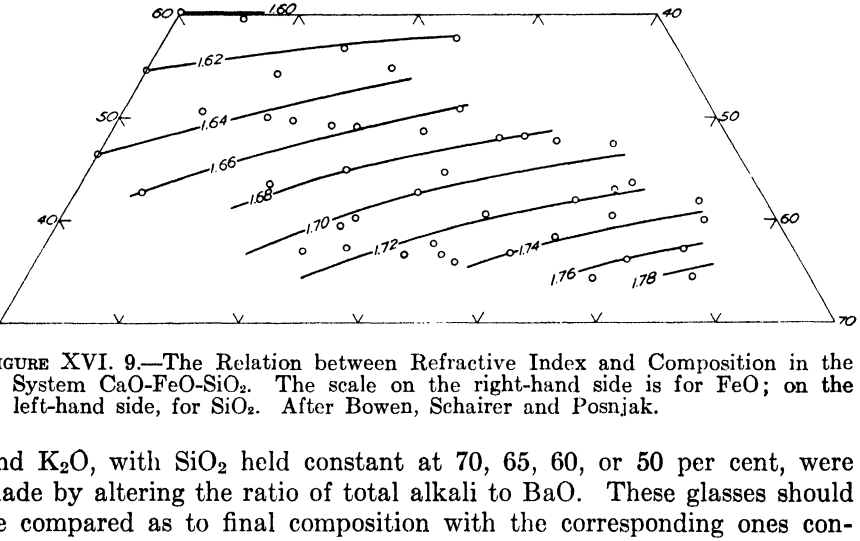

FIGURE XVI. 9.—The Relation between Refractive Index and Composition in the System CaO-FeO-SiO_2. The scale on the right-hand side is for FeO; on the left-hand side, for SiO_2. After Bowen, Schairer and Posnjak.

Na_2O-CaO-Al_2O_3-SiO_2. Larsen [22] measured the refractive indices of glasses on the binary join albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$)—anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$), using lithium ($\lambda = 670.8\,m\mu$), sodium and thallium ($\lambda = 535.0\,m\mu$) light. Measurements were made on prisms by the minimum deviation method, with a probable error of ±0.0003. The composition was correct to 0.3 per cent; the thermal history of the samples was not given. The results are in Table XVI. 13.

Na_2O-K_2O-CaO-B_2O_3-SiO_2. The optical properties of a series of

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[55] Peddle, C. J., *J. Soc. Glass Tech.*, 5, 220, 228 (1921).

glasses of the general formula in percentages by weight: SiO_2, $(75.8 - x)$; B_2O_3, x; CaO, 8.56; Na_2O, 6.86; K_2O, 7.9, measured by Turner and Winks,[39] are given in Table XVI. 10; the analytical compositions of the glasses, in Table X. 3. Measurements were made on a Pulfrich refractometer. Addition of B_2O_3 to the parent four-component glass containing both alkalies, which had properties intermediate between the two three-component glasses containing only one alkali, resulted in the refractive index increasing about 0.025 to a flat maximum near 26 per cent B_2O_3, but in the dispersion remaining about the same. The results are somewhat irregular.

Glasses containing Germanium Dioxide. Dennis and Laubengayer[16] measured the refractive indices of some complex glasses, corresponding in molal batch composition to commercial types, but with GeO_2 replacing SiO_2. The results are in Table XVI. 21. The glasses were not suitable for accurate measurements, especially of dispersion, and the values given in the table probably are accurate only to a few units in the third decimal place in index, or in the fourth decimal place in dispersion.

TABLE XVI. 21—Optical Properties of Some Glasses Containing Germanium Dioxide

After Dennis and Laubengayer

No.	26	27	28	29
Ge_2O	78.50	61.80	60.43	81.48
B_2O_3	7.94	2.34	....	0.17
Na_2O	5.57	....	....	10.11
K_2O	5.74	6.15	4.85	....
CaO	....	....	....	6.59
ZnO	....	7.14	....	....
BaO	2.12	22.20	0.27	....
PbO	....	....	34.12	....
Sb_2O_3	....	....	....	1.32
As_2O_3	0.14	0.36	0.35	0.33
n_C	1.63861	1.68643	1.77210	1.67771
n_D	1.64267	1.69077	1.78001	1.68252
n_F	1.65289	1.70321	1.79979	1.69455
n_G	1.66120	1.71300	1.82932	1.70474
γ	45.0	41.2	28.0	40.5

Multi-component and Optical Glasses

The classification of optical glasses is based on the refractive index and the ν-value, as shown in Fig. XVI. 10, reproduced with slight alterations from the catalog of Schott und Gen. Similar methods of classification are used by other manufacturers and are modifications of the method proposed by Morey.[56] The ordinary crown-flint series con-

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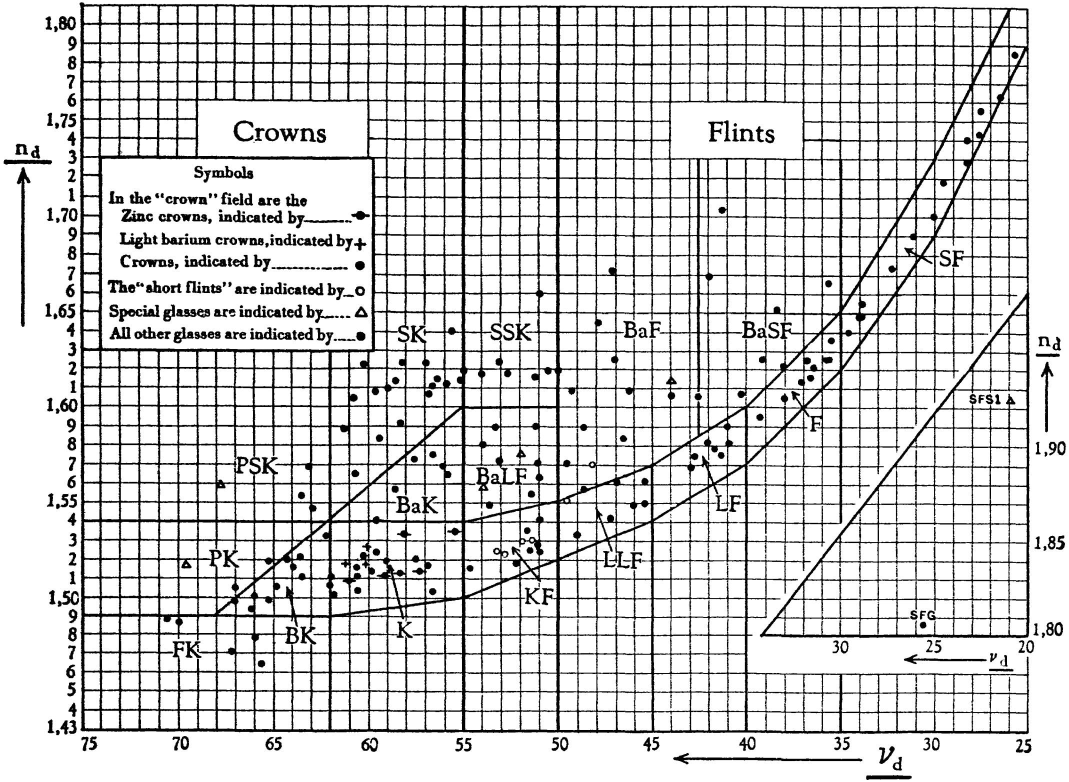
[56] Morey, G. W., *J. Optical Soc. Am.*, **4**, 205 (1920).



The field FK is that of the fluor crowns; K, ordinary crowns; KF, crown-flints or soft crowns; LLF, extra-light flints; LF, light flints; F, flints or medium flints; SF, dense flints; PK, phosphate crowns; PSK, dense phosphate crowns; BaK, light barium crowns; SK, dense barium crowns; SSK, extra-dense barium crowns; BaLF, light barium flints; BaF, barium flints; BaSF, dense barium flints. In the crown field are shown also some light barium crowns, BaLK, and zinc crowns, ZK; and in the crown-flint field are some "short flints," KzF, which have partial dispersion ratios differing from the crown-flints.

FIGURE XVI. 10.—Classification of Optical Glasses, Modified from the Catalog of Jnaer Glaswerk Schott und Gen., Jena.

sists of glasses which have a linear relation between refractive index and dispersion, and the ν-value may be expressed as a function of refractive index,

$$n_D = (1 - b\nu)/(1 - a\nu),$$

in which the constants a and b have the values 0.079 and 0.110, respectively. The details of the subdivision of the diagram into the various fields, the limits of those fields, and the names applied are wholly arbitrary, and some differences exist among manufacturers.

Accurate knowledge of refractive index and dispersion is essential in the calculation of lens formulas, and catalogs of optical glass usually give such information. Table XVI. 22 gives density, n_D, ν-value, partial and relative dispersions, and batch compositions of some glasses manufactured * by Chance Brothers. Table XVI. 23 gives the density, optical data, and batch compositions of some glasses manufactured ** by Parra Mantois et Cie.

Table III. 4 gives partial information for a number of glasses made by Schott und Genössen. In column 2 of that table are given values for $(n_D - 1)$ and 10ν; for example, No. 1, 496/644 means[57] that $n_D = 1.496$, $\nu = 64.4$. The compositions and optical properties of the glasses in Table III. 4 were collected from several sources, and the composition given is usually that of the type of glass, not of the sample on which the measurement was made. Much of the data in that table was taken from the well-known treatise by Hovestadt[58] on the scientific work carried on at Jena by Schott, Winkelmann and their collaborators, and from the article by Zschimmer[59] in Doelter's "Handbuch der Mineralchemie." Most of the data from these two sources has been republished by Wright[60] and by Morey,[61] and some of it by Montgomery.[62] Refractive indices and compositions of some glasses made by the National Bureau of Standards are in Table VI. 2B.

Table XVI. 24 gives the measurements of refractive index for a number of spectral lines ranging from ultra-violet to extreme infra-red, made

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* The above information was furnished me for inclusion in "International Critical Tables." by Chance Bros., Ltd., Smethwick, Birmingham, England, to whom I express my gratitude.

** The above information was furnished me for inclusion in this book by Parra Mantois et Cie., La Vésinet, Paris, France, through the courtesy of B. Long, to whom I express my gratitude.

[57] This convenient method of describing the optical properties of glass was suggested by W. Zschokke, *Z. Instrumentenk.*, **38**, 49 (1918).

[58] Hovestadt, H., "Jenaer Glas und seine Verwendung in Wissenschaft und Technik," Gustav Fischer, Jena, 1900. Translation by Everett, J. D. and A., Macmillan, New York, 1902.

[59] Zschimmer, E., in Doelter, C., "Handbuch der Mineralchemie," **1**, 869, T. Steinkopff, Dresden u. Leipzig, 1912.

[60] Wright, F. E., "The Manufacture of Optical Glass and of Optical Systems," *U. S. Ordnance Dept., Document No.* 2037; Govt. Printing Office, Washington, 1921.

[61] Morey, G. W., "Properties of Glass," **2**, 87, *International Critical Tables;* McGraw-Hill, New York, 1927.

[62] Montgomery, R. J., *J. Am. Ceram. Soc.*, **3**, 900 (1920); **4**, 536 (1921).

TABLE XVI. 22—Properties and Approximate Compositions of

A. Optical Properties

	Type No.	Variety of Glass	n_D	Mean Dispersion C-F	ν	Partial Dispersions and Relative Partial Dispersions			Sp. Gr.
						C-D	D-F	F-G'	
1.	7423	Fluor Crown	1.4785	.00682	70.2	.00202 .296	.00480 .704	.00363 .532	2.47
2.	3484	Boro-silicate Crown	1.4980	.00763	65.3	.00227 .298	.00536 .702	.00425 .557	2.40
3.	646	Boro-silicate Crown	1.5087	.00793	64.1	.00237 .299	.00556 .701	.00445 .561	2.46
4.	6493	Boro-silicate Crown	1.5160	.00809	63.8	.00242 .299	.00567 .701	.00454 .561	2.54
5.	4990	Boro-silicate Crown	1.5100	.00821	62.1	.00246 .299	.00575 .701	.00462 .562	2.50
6.	9753	Dense Barium Crown	1.5881	.00962	61.1	.00287 .298	.00675 .702	.00541 .563	3.31
7.	1203	Hard Crown	1.5155	.00848	60.8	.00250 .295	.00598 .705	.00482 .568	2.48
8.	605	Hard Crown	1.5175	.00856	60.5	.00254 .297	.00602 .703	.00484 .565	2.49
9.	9322	Hard Crown	1.5186	.00860	60.3	.00254 .295	.00606 .705	.00489 .569	2.49
10.	8065	Dense Barium Crown	1.6130	.01025	59.8	.00302 .294	.00723 .706	.00582 .568	3.58
11.	3463	Light Barium Crown	1.5407	.00910	59.4	.00268 .295	.00642 .705	.00517 .568	2.90
12.	4873	Dense Barium Crown	1.6118	.01037	59.0	.00305 .294	.00732 .706	.00590 .569	3.56
13.	1066	Zinc Crown	1.5149	.00890	57.9	.00265 .298	.00625 .702	.00506 .569	2.62
14.	9002	Medium Barium Crown	1.5744	.00995	57.7	.00292 .293	.00703 .707	.00567 .570	3.23
15.	2065	Dense Barium Crown	1.6134	.01090	56.3	.00319 .292	.00771 .708	.00626 .575	3.58
16.	8265	Dense Barium Crown	1.6150	.01097	56.1	.00323 .292	.00776 .708	.00630 .575	3.58
17.	7472	Medium Barium Crown	1.5837	.01041	56.1	.00304 .292	.00737 .708	.00596 .573	3.29
18.	4469	Light Barium Flint	1.5661	.01029	55.0	.00301 .293	.00728 .707	.00591 .574	3.14
19.	4277	Telescope Flint	1.5237	.01003	52.2	.00295 .294	.00708 .706	.00577 .575	2.67
20.	5062	Light Barium Flint	1.5515	.01067	51.7	.00310 .291	.00757 .709	.00619 .581	2.99
21.	7863	Extra Light Flint	1.5290	.01026	51.6	.00300 .292	.00726 .708	.00593 .578	2.56
22.	1078	Light Barium Flint	1.5523	.01075	51.4	.00313 .291	.00762 .709	.00624 .581	3.06
23.	466	Light Barium Flint	1.5833	.01251	46.6	.00362 .289	.00889 .711	.00738 .590	3.30
24.	7983	Light Barium Flint	1.5534	.01201	46.1	.00347 .289	.00854 .711	.00711 .592	2.96
25.	458	Light Flint	1.5472	.01196	45.8	.00348 .291	.00848 .709	.00707 .591	2.93
26.	1018	Light Flint	1.5491	.01206	45.5	.00348 .289	.00858 .711	.00714 .592	2.95
27.	665	Light Barium Flint	1.5677	.01291	44.0	.00371 .288	.00920 .712	.00763 .591	3.08
28.	8653	Light Flint	1.5632	.01312	42.9	.00375 .286	.00937 .714	.00781 .595	3.07
29.	1017	Light Flint	1.5746	.01388	41.4	.00396 .285	.00992 .715	.00830 .598	3.18
30.	407	Light Flint	1.5787	.01420	40.8	.00406 .286	.01014 .714	.00851 .599	3.26
31.	3743	Dense Flint	1.6125	.01655	37.0	.00471 .285	.01184 .715	.01003 .606	3.54
32.	4743	Dense Flint	1.6134	.01662	36.9	.00473 .285	.01189 .715	.01008 .606	3.55
33.	361	Dense Flint	1.6214	.01722	36.1	.00491 .285	.01231 .715	.01047 .608	3.63
34.	4675	Very Dense Barium Flint	1.6683	.01876	35.6	.00533 .284	.01343 .716	.01147 .611	3.98
35.	337	Very Dense Flint	1.6469	.01917	33.7	.00541 .282	.01376 .718	.01170 .610	3.87
36.	4141	Very Dense Flint	1.7167	.02430	29.5	.00686 .282	.01744 .718	.01511 .622	4.47

Some Optical Glasses Manufactured by Chance Bros. and Co., Ltd.

B. Approximate Compositions

	Type No.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	PbO	Al_2O_3	As_2O_3	Sb_2O_3
1.	Fluor Crown*	54.8	18.7		20.3					.3	.2	
2.	3484 B.S.C.	59.5	21.5		14.4	.3		2.3		1.9	.1	
3.	646 B.S.C.	69.6	6.7		20.5	2.9				.3	.1	
4.	6493 B.S.C.	67.1	7.2		16.2	2.0	7.2			.3	.1	
5.	4990 B.S.C.	71.1	2.7		18.8	6.8				.3	.2	
6.	9753 D.B.C.	32.3	19.0		.2	.2	42.3			5.7	.5	
7.	1203 H.C.	69.5			19.0	11.1				.3	.2	
8.	605 H.C.	69.6			18.4	11.5				.3	.2	
9.	9322 H.C.	72.0		6.1	10.1	11.4				.3	.2	
10.	8065 D.B.C.	31.3	15.4		.2	.2	48.7			3.5	.2	.4
11.	3463 L.B.C.	57.1	1.8		13.7	.3	26.9			.2	.1	
12.	4873 D.B.C.	36.2	7.7		.2	.2	44.6	6.7		3.5	.7	.3
13.	1066 Z.C.	69.7		11.0	1.7	.4		16.5		.3	.4	
14.	9002 M.B.C.	45.6	4.4		3.9	.3	32.5	7.9		4.9	.6	
15.	2065 D.B.C.	36.7	5.9		.9	.2	45.1	6.8		3.6	.8	
16.	8625 D.B.C.	36.2	4.7		1.8	.2	45.9	6.7		3.5	.7	.4
17.	7472 M.B.C.	42.6	5.1		9.3	.2	31.4	10.5		.2		.8
18.	4469 L.B.F.	49.3		3.2	9.5	.3	27.2	8.6	.7	.2	.1	.8
19.	4277 T.F.	52.4	18.3	2.3	4.3	.3				1.9	.1	20.4
20.	5062 L.B.F.	55.9			13.3	.3	14.8	4.1	10.7	.2		.7
21	7863 E.L.F.	66.8		9.2	3.9	.4		5.2	7.1	.3	.1	7.0
22.	1078 L.B.F.	56.4			12.0	.3	15.1	4.1	11.1	.2		.7
23.	466 L.B.F.	47.5		3.0	9.1	.3	15.3	8.3	16.3	.2	.1	
24.	7983 L.B.F.	57.7			12.0	.3	4.5		24.9	.2	.1	.3
25.	458 L.F.	59.7			12.6	.3			26.9	.3	.1	
26.	1018 L.F.	60.6			13.9	.3	2.5		22.5	.3	.1	
27.	665 L.B.F.	52.3			9.9	.3	7.4		29.9	.2	.2	
28.	8653 L.F.	55.9			11.1	.3			32.9	.2	.1	
29.	1017 L.F.	52.8			10.1	.3			36.5	.2	.1	
30.	407 L.F.	52.5			9.5	.3			37.5	.2	.1	
31.	3743 D.F.	47.5		5.1	1.2	.3			45.6	.2	.1	
32.	4743 D.F.	48.0		5.2	1.2	.3			45.1	.2	.1	
33.	361 D.F.	46.3		5.0	1.1	.3			47.0	.2	.1	
34.	4675 D.B.F.	36.6			4.9	.2	13.6	4.7	39.2	.2	.2	.6
35.	337 E.D.F.	40.6			7.5	.2			51.5	.2	.1	
36.	4141 D.E.D.F.	35.1			2.8	.1			61.8	.1		

* Also contains 7.5% F.

Table XVI. 23A—Properties of Some Optical Glasses Manufactured by Para-Mantois et Cie.

			Indices of Refraction, for light of wave-length given in Angstroms							Partial Dispersions and Dispersion Ratios							
No.	Type	Density	7682 A'	6563 C	5893 D	5461 e	4861 F	4341 G'	4047 405	Mean Dispersion $F-C$	$\nu = \frac{D-1}{F-C}$	$C - A'$ $C - A'/F - C$	$D - C$ $D - C/F - C$	$e - D$ $e - D/F - C$	$F - e$ $F - e/F - C$	$G' - F$ $G' - F/F - C$	$405 - G'$ $405 - G'/F - C$
A9068	Fluor Crown	2.30	1.48474	1.48738	1.48953	1.45132	1.49457	1.49854	1.50153	0.00719	68.1	0.00264 0.367	0.00215 0.299	0.00325 0.452	0.00328 0.451	0.00397 0.552	0.00299 0.416
B1664	Boro-silicate Crown	2.53	1.51113	1.51397	1.51642	1.51837	1.52205	1.52661	1.53001	0.00808	63.9	0.00284 0.351	0.00245 0.303	0.00195 0.241	0.00368 0.455	0.00456 0.564	0.00340 0.420
B0061	Crown	2.44	1.49490	1.49778	1.50020	1.50226	1.50600	1.51064	1.51416	0.00822	60.9	0.00288 0.350	0.00242 0.294	0.00206 0.251	0.00374 0.455	0.00464 0.564	0.00352 0.428
B3959	Light Barium Crown	2.83	1.53333	1.53647	1.53918	1.54138	1.54553	1.55064	1.55454	0.00906	59.5	0.00314 0.347	0.00265 0.297	0.00219 0.245	0.00409 0.458	0.00506 0.567	0.00381 0.427
B7657	Light Barium Crown	3.23	1.56945	1.57294	1.57591	1.57837	1.58297	1.58866	1.59299	0.01003	57.4	0.00349 0.348	0.00297 0.296	0.00246 0.245	0.00460 0.459	0.00569 0.567	0.00433 0.432
B8761	Dense Barium Crown	3.34	1.58081	1.58417	1.58702	1.58940	1.59379	1.59923	1.60332	0.00962	61.0	0.00336 0.349	0.00285 0.296	0.00238 0.247	0.00439 0.456	0.00544 0.565	0.00409 0.425
C1455	Dense Barium Crown	3.63	1.60671	1.61047	1.61373	1.61645	1.62155	1.62789	1.63276	0.01108	55.4	0.00376 0.339	0.00326 0.294	0.00272 0.245	0.00510 0.460	0.00634 0.572	0.00487 0.440
B2555	High Dispersion Crown	2.63	1.51932	1.52261	1.52543	1.52491	1.53219	1.53771	1.54194	0.00958	54.8	0.00329 0.343	0.00282 0.294	0.00236 0.246	0.00440 0.459	0.00552 0.576	0.00423 0.422
B6555	Light Barium Flint	3.00	1.55868	1.56228	1.56531	1.56786	1.57261	1.57856	1.58313	0.01033	54.7	0.00360 0.348	0.00303 0.293	0.00255 0.247	0.00475 0.460	0.00595 0.576	0.00457 0.442
C1754	Very Dense Barium Crown	3.66	1.60993	1.61374	1.61712	1.61989	1.62513	1.63170	1.63673	0.01139	54.2	0.00381 0.335	0.00338 0.297	0.00277 0.243	0.00524 0.460	0.00657 0.577	0.00503 0.442
B4946	Extra-Light Flint	2.94	1.54202	1.54602	1.54950	1.55246	1.55804	1.56514	1.57064	0.01202	45.7	0.00400 0.333	0.00348 0.290	0.00296 0.246	0.00558 0.464	0.00710 0.591	0.00550 0.458
C5845	Barium Flint	4.05	1.64863	1.65344	1.65767	1.66133	1.66813	1.67685	1.68362	0.01469	44.8	0.00481 0.327	0.00423 0.288	0.00366 0.249	0.00680 0.463	0.00872 0.593	0.00677 0.461
B6843	Light Flint	3.11	1.56017	1.56456	1.56841	1.57169	1.57791	1.58586	1.59209	0.01335	42.6	0.00439 0.329	0.00385 0.288	0.00328 0.246	0.00622 0.466	0.00795 0.596	0.00623 0.467
C1736	Dense Flint	3.59	1.60711	1.61245	1.61731	1.62143	1.62936	1.63967	1.64775	0.01691	36.5	0.00534 0.316	0.00486 0.287	0.00412 0.244	0.00793 0.469	0.01031 0.610	0.00808 0.478
C2637	Dense Flint	3.64	1.61589	1.62140	1.62629	1.63049	1.63851	1.64890	1.65712	0.01711	36.6	0.00551 0.322	0.00489 0.286	0.00420 0.245	0.00802 0.469	0.01039 0.607	0.00827 0.480
C5034	Extra-Dense Flint	3.86	1.63846	1.64455	1.65001	1.65472	1.66378	1.67557	1.68500	0.01923	33.8	0.00609 0.317	0.00546 0.284	0.00471 0.245	0.00906 0.471	0.01179 0.613	0.00943 0.490
C8132	Extra-Dense Flint	4.10	1.66885	1.67550	1.68149	1.68670	1.69671	1.70982	1.72036	0.02121	32.1	0.00665 0.314	0.00599 0.282	0.00521 0.246	0.01001 0.472	0.01311 0.618	0.01054 0.497
C9930	Extra-Dense Flint	4.28	1.68547	1.69267	1.69917	1.70487	1.71581	1.73022	1.74189	0.02314	30.2	0.00720 0.311	0.00650 0.280	0.00570 0.246	0.01094 0.473	0.01441 0.622	0.01167 0.504

by Rubens [63] and by Trommsdorf.[64] The fifth decimal place is uncertain in these measurements. The measurements of Kingslake and Conrady [65] probably are more accurate than those of Rubens and Trommsdorf, and are self-consistent to 5 or 6 in the fifth decimal place. They are given in Table XVI. 25 and are shown in Fig. XVI. 11. The shapes of the curves are similar to those obtained by Rubens, with an inflection at around 1.4 to 1.6μ, in which region the dispersions of all the glasses are about the same.

TABLE XVI. 23B—Approximate Compositions of the Above Glasses

No.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	ZnO	BaO	PbO	Al_2O_3	As_2O_3	Sb_2O_3
A9068(1)	52.90	19.07	17.92						3.76	0.32	
B1664	70.10	10.70	16.02				2.84				0.34
B0061(2)	73.63		19.91		4.76				0.64	0.36	
B3959	54.74	14.05	18.80		0.61		6.80	3.64	1.09		0.27
B7657	46.91	6.33	5.50			11.96	27.17		1.67	0.46	
B8761	37.65	14.87					42.02		5.27		0.19
C1455	37.04	6.15				9.25	42.04	1.26	3.70	0.56	
B2555	68.30	1.50	16.40		3.96			9.50		0.34	
B6555	50.32	10.15	14.35		2.82		13.76	8.35		0.25	
C1754	36.50	5.97				9.42	42.65	1.34	3.57	0.55	
B4946	60.63	0.11	12.45		0.34			25.87		0.30	0.30
C5845	30.54	4.26	2.57			8.12	37.14	14.90		0.30	
B6843	56.58		11.54		0.32			31.28		0.28	
C1736	46.15		8.40		0.52			44.70		0.23	
C2637	45.60	0.83	6.33		0.51			46.50		0.23	
C5034	41.05	0.46	7.63					50.45		0.41	
C8132	37.66		5.26		2.11			54.68		0.29	
C9930	35.40			5.16				59.10		0.34	

(1) Contains 6.03 F. (2) Contains 0.70 F.

The effects of the various oxides commonly used in optical glasses are shown by Fig. XVI. 12, after Merwin. The vertical axis in that figure represents the dispersion $(C - F) \times 10^5$. The horizontal axis consists of two parts. On the left-hand side, the partial dispersion ratio increases from 0.320 to 0.371 (the middle line) for the red end of the spectrum, $(C - A')/(F - C)$; on the right-hand side, the partial dispersion ratio for the violet end of the spectrum, $(h - g)/(F \times C)$, increases from 0.431 (the middle line) to 0.500. Silica glass, for which $(F - C) = 0.00676$, $(C - A')/(F - C) = 0.370$, $(h - g)/(F - C) = 0.433$, is represented by the point indicated. The several pairs of curves in Fig. XVI. 12, representing the glasses of Table XVI. 26, illustrate the differences between the various types of optical glasses.

The optical properties of the glasses used in constructing Fig. XVI. 12 are in Table XVI. 26A. The dispersions of silica glass are interpolated

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[63] Rubens, H., *Ann. Physik Chem.*, **45**, 238 (1892); **53**, 267 (1894); *Sitzber. Kgl. preuss. Akad. Wiss.*, **1916**, II, 1280.

[64] Trommsdorf, H., *Dissertation*, Jena, 1901; *Physik. Z.*, **2**, 576 (1901).

[65] Kingslake, R., and Conrady, H. G., *J. Optical Soc. Am.*, **27**, 257 (1937).

TABLE XVI. 24—Refractive Indices of Several Glasses for Light of Various Wave-lengths

After Rubens (R) *and Trommsdorf* (T)

Source	Wave-length mμ	Number, Table III. 4, or footnote reference, and author												
		60(T)	49(R)	4(T)	N1(R)	12(T)	N2(R)	N2(R)	N3(T)	N4(T)	17(T)	N5(T)	73(R)	22(T)
	2200					1.4943								
	2000		1.4845			1.4967	1.4973						1.5390	
	1800		1.4884			1.4988	1.4999						1.5424	
	1600		1.4919			1.5008	1.5024						1.5452	
	1400		1.4950			1.5027	1.5048						1.5476	
	1200		1.4979			1.5048	1.5069						1.5497	
	1000		1.5009			1.5071	1.5096						1.5522	
	800		1.5044			1.5103	1.5131						1.5555	
K$_{\alpha}$(A^{1})	768		1.50426			1.51143	1.51368	1.51410					1.55651	
H$_{\alpha}$(C)	656.3	1.50486	1.50742	1.50883	1.51436	1.51446	1.51712	1.51742	1.51932	1.52441	1.53755	1.55771	1.55957	1.56014
Cd$_{1}$	643.9	1.50525		1.50917	1.51482				1.51979	1.52490	1.53797	1.55821	1.55821	1.56068
Na(D)	589.0	1.50734	1.51007	1.51124	1.51693	1.51698	1.52002	1.52046	1.52231	1.52704	1.54025	1.56075	1.56207	1.56343
Cd$_{2}$	537.9	1.50976		1.51362	1.51957				1.52536	1.52961	1.54297	1.56375		1.56671
Tl$_{\alpha}$	534.9		1.51287			1.51971	1.52327	1.52363					1.56476	
Cd$_{3}$	533.8	1.51004		1.51386	1.51982				1.52568	1.52989	1.54321	1.56407		1.56689
Cd$_{4}$	508.6	1.51154	1.51447	1.51534	1.52143	1.52132	1.52525	1.52567	1.52754	1.53146	1.54489	1.56596	1.56643	1.56914
H$_{\beta}$(F)	486.1		1.51610	1.51690		1.52299	1.52715	1.52752	1.52954	1.53303			1.56794	1.57148
Cd$_{5}$	479.9	1.51362	1.51662	1.51732	1.52361	1.52354	1.52782	1.52824	1.53007	1.53362	1.54714	1.56844	1.56847	1.57193
Cd$_{6}$	467.8	1.51461	1.51769	1.51828	1.52466	1.52451	1.52903	1.52946	1.53129	1.53464	1.54825	1.56968	1.56949	1.57333
Cd$_{7}$	441.6	1.51704		1.52066	1.52725				1.53436	1.53721	1.55093	1.57268		1.57667
H$_{\gamma}$(G')	398.8	1.52210		1.52546	1.53261			1.53341	1.53521	1.53790			1.57273	1.57764
Cd$_{8}$	434.0	1.51775	1.52092	1.52136		1.52778	1.53312		1.54075	1.54245	1.55646	1.57896		1.58375
Cd$_{9}$	361.2	1.52852	1.53195	1.53156	1.53943	1.53897	1.54664	1.54726	1.54897	1.54911	1.56354	1.58704	1.58330	1.59300
Cd	353.6	1.53010			1.54111					1.55071	1.56525			1.59526
Cd$_{10}$	346.7	1.53157	1.53509	1.53445	1.54272	1.54215	1.55068	1.55132	1.55300	1.55225	1.56689	1.59093	1.58632	1.59754
Cd$_{11}$	340.4	1.53307	1.53660	1.53586	1.54432	1.54369	1.55262	1.55330	1.55504	1.55379	1.56852	1.59279	1.58776	1.59978
Cd	334.5	1.53490							1.55746	1.55565	1.57046	1.59452		1.60248
Cd$_{12}$	328.4	1.53721		1.53982	1.54879				1.56043	1.55804	1.57296	1.59796		1.60593
Cd	326.4	1.53811							1.56157					1.60748
Cd	326.1		1.54046			1.54755	1.55770	1.55838					1.59138	
Cd	323.6	1.53896								1.56004		1.60033		1.60900
Cd	322.1	1.53932		1.54168					1.56311	1.56086	1.57511	1.60081		1.61015
Cd	321.0			1.54204										
Cd	320.2	1.53982		1.54238	1.55089					1.56175	1.57593			1.61189
Cd	318.5	1.54079			1.55175				1.56518	1.56193	1.57830	1.60263		
Cd	315.7			1.54475	1.55414				1.56675			1.60475		
Cd$_{13}$	313.3		1.54444	1.54536	1.55450	1.55159	1.56307	1.56381		1.56343	1.57870			
Cd$_{14}$	308.1		1.54625	1.54839	1.55875	1.55343	1.56558	1.56632		1.56661	1.58293			

N1. "Soft silicate crown," probably differing little from III. 4, No. 12.

N2 and 3. Both glasses are "high dispersion crowns," type 0381. N2 was melt 1151; N3, melt 1250, batch composition Table III. 4, No. 13. The analysis 13a is of type 0381, melt number unknown.

N3 and 4 are described as telescope flint, 02001, and telescope crown, 02388. Their composition is not available. See Chance Bros.' telescope flint. Table XVI. 22. No. 19.

N5. A light barium flint, probably differing little from III. 4, No. 21.

N6. A light barium crown, No. 27, Table III. 4.

Source	Wave-length mμ	Number, Table III. 4, or footnote reference, and author												
		60(T)	49(R)	4(T)	N1(R)	12(T)	N2(R)	N2(R)	N3(T)	N4(T)	17(T)	NS(T)	73(R)	22(T)
Cd	306.5									1.56714				
Cd	298.0		1.55005			1.55723	1.57093	1.57176						
Cd	288.0		1.55437			1.56161								
Cd	283.7		1.55648			1.56372								
Cd	276.3		1.56027			1.56759								

Source	Wave-length mμ	Number, Table III. 4, or footnote reference, and author												
		N6(R)	N6(R)	28(R)	29(T)	31(R)	32(T)	34(R)	37(T)	38(T)	N7(N)	53(T)	43(R)	45(R)
	2400			1.5440							1.6131			1.8286
	2200			1.5463							1.6150		1.7082	1.8310
	2000		1.5515	1.5487							1.6171		1.7104	1.8316
	1800		1.5541	1.5512							1.6193		1.7127	1.8364
	1600		1.5565	1.5535							1.6217		1.7151	1.8396
	1400		1.5588	1.5559							1.6246		1.7180	1.8433
	1200		1.5611	1.5585							1.6277		1.7215	1.8481
	1000		1.5637	1.5615							1.6315		1.7264	1.8541
	800		1.5673	1.5659							1.6373		1.7339	1.8650
$K_a(A^1)$	768	1.56731	1.56782	1.56669		1.57508		1.60277			1.63820		1.73530	1.86702
$H_\alpha(C)$	656.3	1.57073	1.57120	1.57119	1.57568	1.57934	1.58848	1.60644	1.61574	1.62285	1.64440	1.65326	1.74368	1.87893
Cd_1	643.9				1.57619		1.58896		1.61656	1.62356		1.65435		
$Na(D)$	589.0	1.57363	1.57422	1.57524	1.57893	1.58282	1.59144	1.60956	1.62073	1.62750	1.64985	1.65762	1.75130	1.88995
Cd_2	537.9				1.58211		1.59433		1.62578	1.63226		1.66146		
Tl_a	534.9	1.57687	1.57746	1.57973		1.58689		1.61292			1.65601		1.75995	1.90262
Cd_3	533.8				1.58244		1.59463		1.62630	1.63274		1.66185		
Cd_4	508.6	1.57883	1.57938	1.58247	1.58444	1.58941	1.59644	1.61504	1 62952	1.63577	1.65979	1.66423	1.76539	
$H_\beta(F)$	486.1	1.58079	1.58126	1.58515	1.58646	1.59178	1.59825	1.61706			1.66367	1.66670	1.77091	1.91890
Cd_5	479.9	1.58132	1.58188	1.58594	1.58715	1.59257	1.59878	1.61770	1.63396	1.63992	1.66482	1.66742	1.77256	
Cd_6	467.8	1.58253	1.58306	1.58772	1.58848	1.59419	1.59996	1.61891	1.63615	1.64196	1.66725	1.66904	1.77609	
Cd_7	441.6				1.59174		1.60285		1.64162	1.64704		1.67292		
$H_\gamma(G^1)$	434.0	1.58651	1.58710	1.59355	1.59268	1.59920	1.60367	1.62320	1.64319		1.67561	1.67436	1.78800	1.94493
Cd_8	398.8				1.59852		1.60870		1.65333	1.65792		1.68104		
Cd_9	361.2	1.59951	1.60022	1.61388	1.60726	1.61691	1.61622	1.63683	1.66933	1.67269	1.70536	1.69146	1.83263	
Cd	353.6				1.60937		1.61800		1.67346			1.69400		

TABLE XVI. 24—*(Continued)*

Source	Wave-length mμ	Number, Table III. 4, or footnote reference, and author												
		N6(R)	N6(R)	28(R)	29(T)	31(R)	32(T)	34(R)	37(T)	38(T)	N7(N)	53(T)	43(R)	45(R)
Cd_{10}	346.7	1.60326	1.60399	1.62008	1.61148	1.62228	1.61978	1.64077	1.67753	1.68018	1.71485	1.69648	1.84731	
Cd_{11}	340.4	1.60510	1.60583	1.62320	1.61356	1.62492	1.62148	1.64271	1.68160	1.68390	1.71968	1.69892	1.85487	
Cd	334.5				1.61559		1.62356		1.68685	1.68838		1.70135		
Cd_{12}	328.4				1.61922		1.62622		1.69265	1.69454		1.70408		
Cd	326.4				1.62069				1.69356			1.70562		
Cd	326.1	1.60973	1.61045	1.63134		1.62166		1.64754			1.73245			
Cd	323.6				1.62159									
Cd	322.1													
Cd	321.0													
Cd	320.2				1.62256									
Cd	318.5				1.62311									
Cd	315.7				1.62462									
Cd_{13}	313.3	1.61446	1.61525	1.64024	1.62678	1.63908		1.65254						
Cd_{14}	308.1	1.61664	1.61744	1.64453		1.64258								
Cd	306.5													
Cd	298.0	1.62122	1.62213	1.65397										
Cd	288.0	1.62642	1.62742											
Cd	283.7	1.62893	1.62997											
Cd	276.3													

Number 43(R)

Wave-length mμ	n	Wave-length mμ	n
4.12	1.6688	936	1.7276
3.83	1.6758	769.93	1.735000
3.56	1.6821	656.33	1.743488
3.24	1.6885	589.32	1.751094
2.98	1.6934	534.96	1.759751
2.71	1.6980	486.16	1.770658
2.40	1.7029	434.09	1.787782
2.02	1.7086	404.44	1.801758
1.625	1.7144		
1.216	1.7208		

N6. Different samples of a light barium crown similar to Table III. 4, Nos. 17 and 17A, of batch composition: SiO_2, 47.8; B_2O_3, 4.5; Na_2O, 1.0; K_2O, 7.5; BaO, 28.5; ZnO, 10.3; Mn_2O_3, 0.1; As_2O_5, 0.5.

N7. Heavy silicate crown, Type 0102, near Table III. 4, No. 40, batch composition: SiO_2, 40.0; Na_2O, 0.5; K_2O, 6.5; PbO, 52.6; Mn_2O_3, 0.09; As_2O_5, 0.1.

TABLE XVI. 25—Refractive Indices of Some Optical Glasses in the Infra-Red

After Kingslake and Conrady

Glass No.	1	2	3	4	5	6	7	8	9	10	11
Maker	B-L[1]	B-L	PM[2]	B-L	B-L	PM	B-L	PM	B-L	Schott	B-L
Type No.	70	20–2	5951	160–1	110–1	6581	120–1	4887	120–2	F2	220–3
Name	Hard Crown	Boro-silicate Crown	Extra-Light Flint	Tele-scope Flint	Dense Barium Crown	Light Flint	Dense Barium Crown	Light Barium Flint	Dense Barium Crown	Dense Flint	Extra-Dense Flint
N_D	1.51166	1.51666	1.52390	1.52970	1.57136	1.57348	1.61173	1.60535	1.61703	1.62082	1.71968
$N_F—N_C$	0.00845	.00802	.01039	.01028	.00995	.01338	.01037	.01381	.01141	.01707	.02454
ν	60.6	64.4	50.4	51.5	57.4	42.9	59.0	43.8	54.1	36.4	29.4
Wave-length:											
0.3650μ	1.53245	(?)	1.55052	1.55555	1.59610	1.60880	1.63738	1.64171	1.64570	1.66714	(absorbed)
h .4046	1.52597	1.53013	1.54192	1.54736	1.58837	1.59718	1.62935	1.62975	1.63666	1.65163	1.76506
G' .4340	1.52239	1.52676	1.53728	1.54286	1.58407	1.59098	1.62491	1.62338	1.63164	1.64346	1.75270
g .4358	1.52217	1.52657	1.53703	1.54262	1.58382	1.59064	1.62467	1.62300	1.63138	1.64300	1.75205
F .4861	1.51760	1.52227	1.53125	1.53695	1.57838	1.58300	1.61903	1.61516	1.62508	1.63307	1.73732
e .5461	1.51375	1.51864	1.52645	1.53224	1.57380	1.57678	1.61429	1.60870	1.61982	1.62503	1.72569
D .5893	1.51166	1.51666	1.52390	1.52970	1.57136	1.57348	1.61173	1.60535	1.61703	1.62082	1.71968
C .6563	1.50915	1.51425	1.52086	1.52667	1.56843	1.56962	1.60866	1.60135	1.61367	1.61600	1.71278
.60	1.51123	1.51623	1.52336	1.52913	1.57081	1.57280	1.61118	1.60456	1.61638	1.62005	1.71842
.65	1.50937	1.51447	1.52112	1.52688	1.56867	1.56997	1.60891	1.60163	1.61394	1.61632	1.71330
.70	1.50789	1.51302	1.51934	1.52507	1.56690	1.56764	1.60709	1.59930	1.61196	1.61358	1.70935
.75	1.50659	1.51179	1.51788	1.52357	1.56542	1.56583	1.60557	1.59740	1.61030	1.61126	1.70608
.80	1.50548	1.51070	1.51658	1.52230	1.56420	1.56422	1.60423	1.59581	1.60890	1.60936	1.70358
.85	1.50458	1.50978	1.51548	1.52117	1.56314	1.56290	1.60312	1.59445	1.60773	1.60780	1.70140
.90	1.50373	1.50893	1.51454	1.52015	1.56217	1.56172	1.60212	1.59324	1.60668	1.60635	1.69956
.95	1.50299	1.50818	1.51367	1.51927	1.56137	1.56066	1.60123	1.59222	1.60576	1.60517	1.69794
1.00	1.50229	1.50745	1.51289	1.51844	1.56063	1.55975	1.60039	1.59128	1.60493	1.60408	1.69651
1.1	1.50104	1.50613	1.51147	1.51689	1.55921	1.55812	1.59891	1.58966	1.60343	1.60220	1.69408
1.2	1.49985	1.50484	1.51021	1.51547	1.55795	1.55663	1.59748	1.58823	1.60205	1.60055	1.69199
1.3	1.49873	1.50359	1.50902	1.51413	1.55683	1.55531	1.59624	1.58699	1.60083	1.59911	1.69028
1.4	1.49768	1.50238	1.50784	1.51288	1.55573	1.55403	1.59500	1.58578	1.59970	1.59779	1.68866
1.5	1.49665	1.50114	1.50677	1.51158	1.55465	1.55282	1.59380	1.58464	1.59854	1.59652	1.68725
1.6	1.49557	1.49993	1.50566	1.51028	1.55355	1.55160	1.59258	1.58350	1.59746	1.59523	1.68585
1.7	1.49450	1.49862	1.50455	1.50896	1.55244	1.55040	1.59132	1.58239	1.59629	1.59405	1.68452
1.8	1.49342	1.49732	1.50340	1.50758	1.55133	1.54917	1.59007	1.58128	1.59515	1.59284	1.68315
1.9	1.49221	1.49592	1.50222	1.50613	1.55016	1.54785	1.58870	1.58008	1.59396	1.59155	1.68181
2.0	1.49094	1.49446	1.50096	1.50460	1.54896	1.54647	1.58732	1.57887	1.59268	1.59026	1.68040
2.1	1.48968	1.49291	1.49965	1.50303	1.54767	1.54506	1.58588	1.57761	1.59140	1.58893	1.67902
2.2	1.48836	1.49132	1.49831	1.50141	1.54634	1.54364	1.58438	1.57636	1.59001	1.58753	1.67763
2.3	1.48697	1.48959	1.49693	1.49967	1.54497	1.54216	1.58276	1.57502	1.58865	1.58612	1.67618
2.4	1.48549	1.48783	1.49546	1.49778	1.54348	1.54059	1.58107	1.57357	1.58714	1.58465	1.67474
2.5	1.48394	1.48597	1.49393	1.49588	1.54197	1.53901	1.57931	1.57218	1.58566	1.58314	1.67315
2.6	1.48234	1.48384	1.49226	1.49378	1.54037	1.53727	1.57747	1.57066	1.58403	1.58147	1.67149

[1] Bausch and Lomb

[2] Parra-Mantois

from the values given by Sosman[15] and the later results of Tilton and Tool.[66] The properties of S 52 are partly interpolated, partly extrapolated from the data given by Hovestadt.[58] The optical properties for the rest of the glasses are from Catalog 5858 g of the Jenaer Glaswerk, Schott und Gen. The compositions of most of these glasses are not available. Some composition references are in Table XVI. 26B; the qualitative compositions are from Eitel, Pirani, and Scheel.[67]

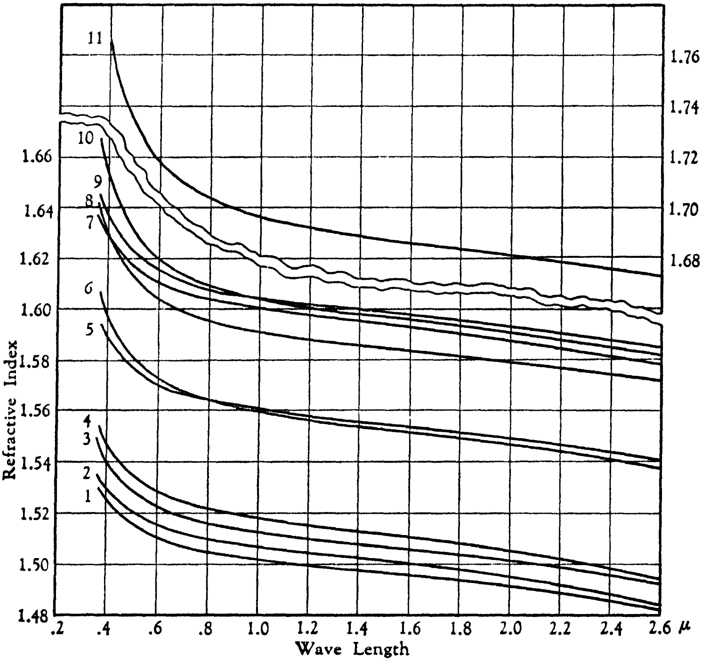

FIGURE XVI. 11.—Dispersion Curves of Eleven Optical Glasses. After Kingslake and Conrady.

The pair of curves *1-1* (Fig. XVI. 12) represents glasses obtained by adding Na_2O, K_2O, ZnO, Sb_2O_3, and PbO to SiO_2, and thus includes the ordinary soft crown-zinc crown-ordinary flint series of glasses, for which the red end of the spectrum is extremely short and the violet end extremely long. Fluorine in the minor amounts reported for this series increases the violet ratio by 0.002 to 0.003, and the aluminum oxide used with it appears to cause a similar increase in the red dispersion ratio.

The curves *2-2* represent the borate flints, and a downward extension

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[66] Tilton, L. W., and Tool, A. Q., *Bur. Standards J. Research,* 3, 619 (1929).

[67] Eitel, W., Pirani, M., and Scheel, K., "Glastechnische Tabellen und Chemische Konstanten der Gläser," J. Springer, Berlin, 1932.

would include *2a*, a borate crown. These glasses are highest in boric oxide, and their dispersion ratios for red are the highest, for violet almost the lowest, of all glasses. Dispersion increases from the low value for the borate crown, which is chiefly Al_2O_3 and B_2O_3, to the high value for the borate flint, which is chiefly PbO and B_2O_3; intermediate glasses may contain large amounts of ZnO and BaO, or both. Boric oxide is

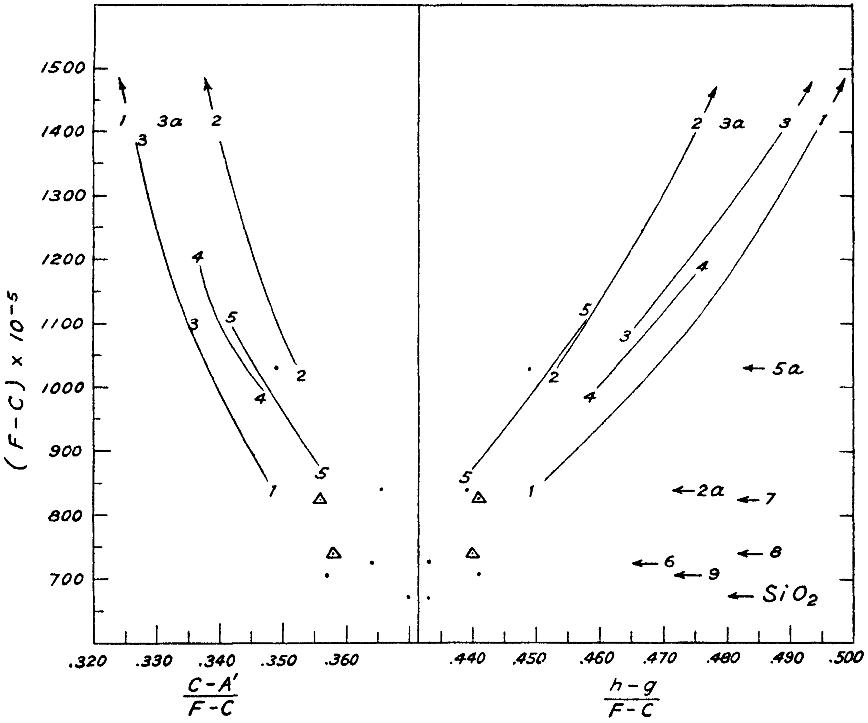

FIGURE XVI. 12.—The Relation between Dispersion and Composition of Optical Glasses. The vertical axis consists of two parts; on the left-hand side, the partial dispersion ratio for the red end of the spectrum, $(C-A')/(F-C)$, increasing from 0.320 to 0.371 (the middle line); on the right-hand side, the partial dispersion ratio for the violet, $(h-g)/(F-C)$, from 0.341 (the middle line) to 0.500. After Merwin.

almost entirely responsible for the lengthened red spectrum, and aluminum oxide has a similar but smaller effect. Boric oxide also is chiefly responsible for the shortened violet spectrum, but BaO has a similar effect when it replaces PbO in a silicate flint (see *3-3* below).

Curves *3-3* show that the effect of 20 per cent (at $F-C$, 0.01000) is 16 per cent (at $F-C$, 0.01400) of BaO on a lead-zinc silicate flint is to decrease relatively the ratio $(h-g)/(F-C)$ without changing the

TABLE XVI. 26A—Properties of Optical Glasses Made by Schott und Genössen Used in Constructing Fig. XVI. 12.

Curve Fig. XVI. 12	Name	Type	Density	n_d	ν_d	Mean Dispersion $F - C$	Partial Dispersions and Dispersion Ratios $C - A'$ $C - A'/F - C$	$e - C$ $e - C/F - C$	$F - e$ $F - e/F - C$	$g - F$ $g - F/F - C$	$h - g$ $h - g/F - C$	Refractive Indices n_C	n_d $n_D - n_d$ (−)	n_g $n_{G'} - n_g$ (+)
	Silica Glass		2.20	1.458_7	67.9	0.00676	0.00250 0.370	0.00372 0.551	0.00304 0.450	0.00357 0.529	0.00292 0.433			
1-1	Crown	K6	2.43	1.5028	60.6	0.00830	0.00289 0.348	0.00451 0.543	0.00379 0.457	0.00450 0.542	0.00373 0.450	1.50023	1.50276 0.00008	1.51303 0.00019
1-1	Crown-Flint	KF2	2.72	1.5263	51.0	0.01032	0.00349 0.338	0.00557 0.540	0.00475 0.460	0.00573 0.556	0.00484 0.469	1.52318	1.52630 0.00010	1.53923 0.00025
1-1	Light Flint	LF7	3.22	1.5750	41.3	0.01392	0.00455 0.327	0.00743 0.534	0.00649 0.466	0.00799 0.574	0.00686 0.493	1.57089	1.57501 0.00012	1.59280 0.00035
1-1	Light Flint	LF5	3.25	1.5814	40.8	0.01425	0.00462 0.324	0.00760 0.533	0.00665 0.467	0.00818 0.575	0.00703 0.494	1.57722	1.58144 0.00013	1.59964 0.00035
2-2	Special Short Flint	KzFS2	2.74	1.5578	53.9	0.01036	0.00364 0.352	0.00563 0.543	0.00473 0.457	0.00563 0.544	0.00471 0.454	1.55465	1.55781 0.00009	1.57064 0.00025
2-2	Special Short Flint	KzFS1	3.17	1.6131	44.0	0.01393	0.00473 0.340	0.00750 0.538	0.00643 0.462	0.00779 0.559	0.00661 0.475	1.60887	1.61306 0.00012	1.63059 0.00034
2a		S52	2.24	1.5048	60.0	0.00840	0.00307 0.366	0.00462 0.550	0.00378 0.450	0.00447 0.532	0.00369 0.439			
3-3	Light Barium Flint	BaLF3	3.16	1.5714	53.0	0.01079	0.00363 0.336	0.00581 0.539	0.00498 0.461	0.00598 0.554	0.00502 0.465	1.56810	1.57135 0.00010	1.58487 0.00025
3-3	Light Barium Flint	BaLF4	3.18	1.5796	53.9	0.01076	0.00366 0.341	0.00581 0.540	0.00495 0.460	0.00594 0.552	0.00497 0.462	1.57632	1.57957 0.00010	1.59302 0.00026
3a	Barium Flint	BaF10	3.84	1.6700	47.2	0.01420	0.00471 0.332	0.00761 0.536	0.00659 0.464	0.00801 0.564	0.00681 0.480	1.66580	1.67003 0.00013	1.68801 0.00035
4-4	Short Flint	KzF5	2.49	1.5213	52.8	0.00988	0.00343 0.347	0.00535 0.542	0.00453 0.458	0.00541 0.548	0.00453 0.459	1.51830	1.52130 0.00009	1.53359 0.00024
4-4	Short Flint	KzF4	3.03	1.5704	48.1	0.01185	0.00400 0.337	0.00637 0.538	0.00548 0.462	0.00665 0.561	0.00565 0.476	1.56686	1.57041 0.00010	1.58536 0.00029
5-5	Heavy Phosphate Crown	PSK3	2.91	1.5523	63.5	0.00870	0.00310 0.356	0.00474 0.545	0.00396 0.455	0.00466 0.536	0.00383 0.440	1.54966	1.55232 0.00008	1.56302 0.00020
5-5	Heavy Crown	SK10	3.66	1.6228	56.9	0.01095	0.00374 0.342	0.00592 0.541	0.00503 0.459	0.00600 0.548	0.00501 0.458	1.61949	1.62280 0.00010	1.63644 0.00026
5a	Heavy Crown	SK16	3.60	1.6204	60.3	0.01029	0.00360 0.349	0.00559 0.543	0.00470 0.457	0.00557 0.541	0.00462 0.449	1.61728	1.62041 0.00010	1.63314 0.00025
6	Fluor Crown	FK4	2.23	1.4783	65.9	0.00726	0.00234 0.364	0.00398 0.549	0.00328 0.451	0.00384 0.529	0.00315 0.433	1.47603	1.47828 0.00006	1.48713 0.00017
7	Special Heavy Prosphate Crown	PSKS1	3.10	1.5582	67.8	0.00824	0.00294 0.356	0.00450 0.546	0.00374 0.454	0.00440 0.534	0.00363 0.441	1.55570	1.55823 0.00007	1.56834 0.00019
8	Special Phosphate Crown	PKS1	2.57	1.5173	69.6	0.00743	0.00266 0.358	0.00407 0.547	0.00336 0.453	0.00397 0.534	0.00327 0.440	1.51499	1.51728 0.00006	1.52639 0.00017
9	Fluor Crown	FK3	2.28	1.4645	65.7	0.00706	0.00252 0.357	0.00386 0.547	0.00320 0.453	0.00378 0.535	0.00311 0.441	1.46232	1.46450 0.00006	1.47317 0.00016

corresponding ratio $(C - A')/(F - C)$. Barium flints containing boric oxide, and others of unknown composition, appear between *3a* and *3-3*, *5-5*, and *2-2*.

The borosilicate flints are intermediate between the borate flints (*2-2*) and the silicate flints (*1-1*). The curves *4-4* are for a series in which the lower members contain antimony oxide in place of lead oxide.

The curves *5-5* represent essentially barium borate and silica; No. *6*, potassium borate and silica. The second of these shows the lengthened red and the shortened violet spectra caused by boric oxide; the first of these shows also the added effect of barium oxide in shortening the violet, which effect is most extreme in *5a*, a heavy crown of unrecorded composition.

TABLE XVI. 26B—Compositions of the Glasses, Table XVI. 26A

	Less than 10 per cent	More than 10 per cent
K6	Na_2O, CaO, Al_2O_3 (1%), As_2O_3	SiO_2, Na_2O
KF2	Table III. 4, No. 13	
LF7	Na_2O, K_2O, As_2O_3	SiO_2, PbO
LF5	Na_2O, K_2O, As_2O_3	SiO_2, PbO
KzFS2	SiO_2, K_2O, PbO, Al_2O_3, As_2O_3	B_2O_3, ZnO
KzFS1	Al_2O_3, As_2O_3	B_2O_3, PbO
S52	Na_2O, BaO, As_2O_3	B_2O_3, Al_2O_3
BaLF3	Table III. 4, No. 24	
BaLF1	Table III. 4, No. 33	
KzF5	Na_2O, K_2O, Al_2O_3, As_2O_3	SiO_2, B_2O_3, Sb_2O_3
KzF4	Na_2O, K_2O, Al_2O_3, As_2O_3	SiO_2, B_2O_3, PbO
SK10	ZnO, PbO, Al_2O_3, As_2O_3	SiO_2, B_2O_3, BaO
SK16	Na_2O, Al_2O_3, Sb_2O_3, As_2O_3	SiO_2, B_2O_3, BaO
FK4	K_2O, As_2O_3	SiO_2, B_2O_3
PSKS1	B_2O_3, Al_2O_3, As_2O_3	P_2O_5, BaO
PKS1	B_2O_3, MgO, Al_2O_3, As_2O_3	P_2O_5, K_2O
FK3	As_2O_3, F	SiO_2, B_2O_3, K_2O, Al_2O_3

No. *7* is a barium phosphate with aluminum oxide, and *8a*, potassium phosphate with aluminum and magnesium oxides. The dispersion would scarcely be different if silica in proper proportions to give the same dispersion $(F - C)$ could be used.

The effect of six to nine per cent of fluorine in an alkali-aluminum borosilicate glass is to decrease the dispersion $(F - C)$ decidedly without greatly changing the partial dispersion ratios. No. *9* is such a glass.

EFFECT OF TEMPERATURE ON REFRACTIVITY

The effect of change of temperature on refractive index and dispersion, which is of importance in precise refractometry, has been studied from that standpoint by Hastings,[68] by Gifford,[69] and by Tilton.[70]. The

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[68] Hastings, C. S., *Am. J. Sci.*, **15**, 269 (1878).

[69] Gifford, J. W., *Proc. Roy. Soc. (London)*, *A*, **91**, 319 (1915); *A*, **100**, 621 (1922).

[70] Tilton, L. W., *J. Research Natl. Bur. Standards*, **14**, 393 (1935).

temperature coefficient of refractive index is small, ranging from -3×10^{-6} for a fluor crown glass, and 5 and 9×10^{-6} for Pyrex and silica glass, respectively, to 14×10^{-6} for heavy flint glass. Measurements at ordinary temperatures are usually reduced to glass and air temperatures of 15° C.; at high temperatures the measurements are usually reduced to an air temperature of 15° C., or better to vacuum.

Silica glass. Sosman [15] recalculated to absolute indices the results of Rinne,[71] which extend from − 160° to + 1000° C., for four visible frequencies of helium. His table is reproduced as Table XVI. 27. "In the three curves which are carried to 1000°, there is an easily observed irregularity in the vicinity of 600°, which is reminiscent of the less marked irregularity in the dilatation of vitreous silica in this same region, and which is suggestively near the inversion-temperature of quartz. It is too large, and also too uniformly present in the three curves, to be due to errors of measurement in the index, although it is conceivably explainable by a concealed error in the temperature. Additional measurements in this vicinity would be interesting."

TABLE XVI. 27—Absolute Index of Refraction of Silica Glass at Various Temperatures.*

Temp. (° C)	He blue $\lambda = 471.315$ mμ	He green 501.568	He yellow 587.563	He red 667.815
− 160	1.4635	1.4617	1.4581	1.4559
− 64	1.4641	1.4624	1.4586	1.4563
18	1.4649	1.4629	1.4592	1.4569
130	1.4660	1.4642	1.4604	1.4579
235	1.4675	1.4654	1.4616	1.4591
365	1.4692	1.4672	1.4633	1.4608
475	1.4708	1.4689	1.4649	1.4625
590	1.4722	1.4703	1.4663	1.4639
1000		1.4772	1.4729	1.4706

* Calculated by Sosman from the data of Rinne.

Commercial glasses. Measurements at temperatures up to about 100° C. were made by Pulfrich [72] on a series of 12 glasses, and Reed [73] extended the measurements up to the annealing temperatures for some of the same glasses and for additional ones. Their combined results are in Table XVI. 28. Measurements were made by the prism method, using the *C*, *D*, and *F* lines, and *G″*, the λ-line of *Hg*. The values given are the mean change of index per degree, $\times 10^5$, for the interval indicated by the mean temperature, usually about 100°. The refractive indices usually increased with temperature; but in the cases in which it decreased, the amount of decrease was less than that to be expected from the decrease in density. In all cases the dispersion increased with

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[71] Rinne, F., *Neues Jahrb. Mineral., Geol., Beilage Bd.*, **39**, 388 (1914).

[72] Pulfrich, C., *Ann. Physik Chem.*, **45**, 609 (1892).

[73] Reed, J. O., *Ann. Physik Chem.*, **65**, 707 (1898).

TABLE XVI. 28—Effect of Change in Temperature on the Absolute Refractive Index of Glass

After Pulfrich (P) *and Reed* (R)

No. in Table III. 4	Mean temp. (° C)	Change in refractive index, $10^5\ \Delta n/\Delta t$ $\Delta t = \pm 50°$ *C*	*D*	*F*	*G′*
6	52.8	+0.110	+0.137	+0.178	+0.213(P)
11	59.3	−0.129	−0.105	−0.060	−0.010(P)
19	59.2	+0.267	+0.299	+0.356	+0.410(P)
25	58.0	+0.226	+0.250	+0.307	+0.360(R)
	149.6	+0.324	+0.362	+0.456	+0.548
	251.5	+0.509	+0.568	+0.666	+0.768
	351.5	+0.577	+0.639	+0.751	+0.870
	436.5	−1.861	−1.720	−1.504	−1.329
26	56.5	+0.014	+0.045	+0.107	+0.150(R)
	157.1	0.094	0.111	0.179	0.246
	261.5	0.144	0.167	0.249	0.355
	357.0	0.217	0.249	0.350	0.461
27	61.2	0.024	0.035	0.092	0.099
	154.0	0.096	0.113	0.152	0.186
	257.0	0.156	0.174	0.223	0.258
	358.0	0.221	0.247	0.297	0.340
34	55.9	0.394	0.410	0.504	0.528(R)
	148.0	0.419	0.444	0.543	0.517
	251.0	0.455	0.489	0.603	0.629
	356.5	0.509	0.555	0.648	0.682
36	55.1	0.244	0.281	0.389	0.503(P)
43	57.7	0.703	0.778	1.058	1.294(R)
	126.0	0.916	1.051	1.302	1.668
	176.5	0.960	1.092	1.430	1.714
	231.0	1.127	1.237	1.632	1.993
	280.5	1.277	1.396	1.790	2.140
	325.0	1.382	1.544	1.960	2.405
	379.0	1.758	1.904	2.263	2.893
45	60.5	1.119	1.278	1.752	2.161(R)
	125.5	1.275	1.442	1.959	2.477
	177.5	1.379	1.594	2.098	2.617
	250.5	1.577	1.783	2.396	2.992
	330.0	1.808	2.027	2.753	
47	62.6	1.218	1.472	2.110	2.800(R)
	156.2	1.579	1.809	2.536	
	233.0	1.928	2.251	3.212	
	281.0	1.591	1.911	2.918	
48	60	−0.066	−0.074	−0.033	−0.003(P)
70	58.1	−0.202	−0.190	−0.168	−0.142(P)
74	60.3	−0.314	−0.305	−0.246	−0.237(P)

temperature, and the run of dispersion was changed. Pulfrich concluded that the ultra-violet absorption band increases in intensity and shifts toward the visible region as the temperature is increased. This explanation is in harmony with the fact that glasses rich in lead oxide, yellow at ordinary temperatures, are dark red or brown at softening temperatures. He found that cooling in a mixture of ether and carbon dioxide snow further lightened the color of heavy flint glasses. When the heavier flints were heated the *G″* line disappeared completely, as indicated in the table. With the lighter flints, the index rose to a

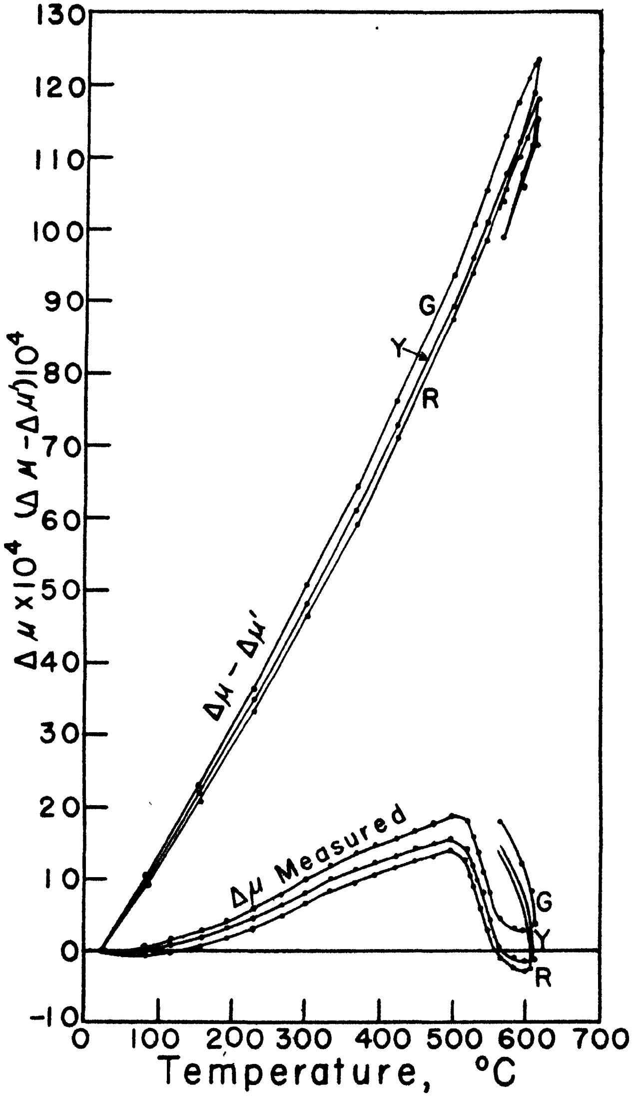

FIGURE XVI. 13.—Change in Refractive Index with Temperature of a Barium Flint Glass. (Compare Fig. XI. 1.) After Peters.

maximum, then decreased, a phenomenon more fully studied by Peters. The dispersion, however, continued to increase.

Peters[74] measured the change of refractive index for a series of glasses

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[74] Peters, C. G., *Bur. Standards Scientific Papers*, 521 (1926).

previously studied by Peters and Cragoe.[75] The glasses were heated at a uniform rate of 2° per minute. The refractive index increased uniformly up to the annealing region, which was about 500° for all the glasses examined. As the glasses passed through the annealing region the rapid increase in expansivity was accompanied by a rapid decrease in the observed index. The results are given as curves, showing the change in refractive index, Δn, for the green ($\lambda = 501.7\,\mathrm{m}\mu$), yellow ($\lambda = 587.7\,\mathrm{m}\mu$), and red ($\lambda = 668.0\,\mathrm{m}\mu$) lines of helium; the expansion; and a quantity $(\Delta n - \Delta n')$ which represents the difference between the observed refractive indices and those calculated from the change in density, assuming the Gladstone-Dale law $[(n - 1)/d] =$ constant. One of the figures given by Peters is reproduced as Fig. XVI. 13. He said: "It seems probable that the measured increase in the index is the result of two opposing effects, a decrease caused by a diminution in density and an increase caused by the augmented absorption. It might be more nearly correct, however, to say that this increase in index and in absorption were both produced by the same or similar causes."

Effect of Pressure on Optical Properties

Theoretical

In considering the effect of pressure on the refractive index of glass, two cases are to be distinguished; in the first, the glass is acted upon by a uniform hydrostatic pressure, and in the second, by non-uniform pressure, resulting from a thrust or tension. The first case is of little practical importance, and the results of uniform compression may be calculated from those obtained in the second and more important case. It is of the effect of a non-uniform pressure that the experimental measurements have been made. The results so obtained are applicable directly to the strains which are introduced into glass by too rapid cooling, and removed by annealing.

When a block of glass is strained, it becomes doubly refracting, and when viewed in polarized light between crossed nicols, it shows interference colors. Brewster [76] showed that under stress the glass behaves as a uniaxial optically negative crystal, and the birefringence is proportional to the intensity of the stress. This phenomenon is the basis of the method in common use for the detection and estimation of stress in glass.

The elementary theory of the effect of stress on birefringence may be outlined [77] as follows. A cube of glass, Fig. XVI. 14, is acted on by a vertical thrust, P, parallel to OY; consider the effect on light passing through the cube in the direction parallel to OX. The effect of the

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[75] Peters, C. G., and Cragoe, C. H., *Bur. Standards Scientific Papers*, **393** (1920).

[76] Brewster, D., *Trans. Roy. Soc. (London) A*, 1814, 1815, 1816.

[77] This discussion follows closely that of Adams, L. H., and Williamson, E. D., *J. Wash. Acad.*, **9**, 609-623 (1919).

thrust *P* will be to compress the glass in the direction *OY*, and to extend it in equal amounts in the directions *OX* and *OZ*. The velocity of the light will be altered, and in general the wave will be split into two wave fronts proceeding with different velocities and polarized in directions at right angles to each other. A ray of polarized light after passing through the block of glass in a direction normal to the direction of thrust, *OY*, will remain a single ray but will be elliptically polarized, and may be treated as the resultant of two rays vibrating, respectively, along *OY* and *OZ* and differing in phase. A thrust parallel to *OZ* will produce an effect similar to that parallel to *OY*, but a thrust parallel to *OX* will produce no phase difference in the rays vibrating along *OY* and *OZ*, since the cube is extended the same amount in these two directions. It follows, then, that when a beam of light passes through a block of strained glass, the velocity of the light, and hence the refractive index of the glass, depends on the direction of vibration of the light and on the dilatations in the directions perpendicular to the path of the beam of light.

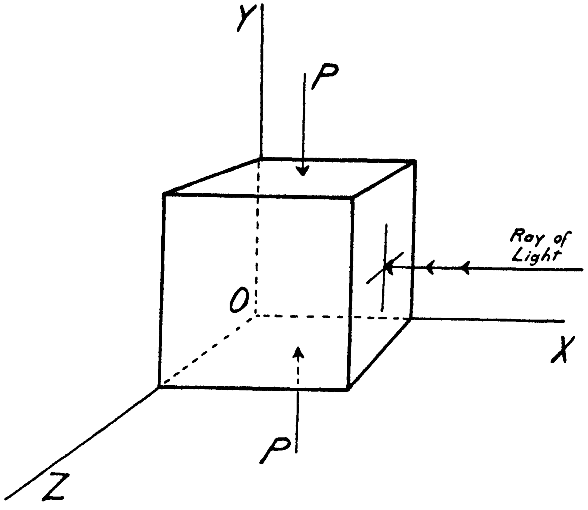

FIGURE XVI. 14.—Diagram to Accompany Explanation in Text of the Effect of Strain in Glass on a Beam of Polarized Light. After Adams and Williamson.

The equations used by Neumann[78] for expressing the influence of elastic deformation on the propagation of light are as follows:

$$v_x = v + qx_x + py_y + pz_z \qquad (1_A)$$

$$v_y = v + px_x + qy_y + pz_z \qquad (1_B)$$

$$v_z = v + px_x + py_y + qz_z \qquad (1_C)$$

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[78] Neumann, F., *Ann. Physik Chem.*, **54**, **449** (**1841**).

in which x_x, y_y, and z_z are dilatations in the three directions parallel to the three principal axes, v is the velocity of light in the unstressed material; v_x, v_y, and v_z are the velocities of light waves whose vibrations are parallel to the three axes; and p and q are coefficients to be determined by experiment.

If n is the refractive index of the unstressed medium and n_x, n_y, and n_z are the refractive indices for light vibrating in the three principal directions, then $nv = n_xv_x = n_yv_y = n_zv_z$, and from Equation (1A)

$$\frac{v_x - v}{v} = \frac{n - n_x}{n_x} = \frac{q}{v}x_x + \frac{p}{v}(y_y + z_z). \tag{2}$$

A thrust, P, acting on the block in the direction OY (Fig. XVI. 14) will produce the three principal dilatations:

$$\begin{aligned} x_x &= \sigma P/E \\ y_y &= -P/E \\ z_z &= \sigma P/E \end{aligned}$$

E being Young's modulus and σ Poisson's ratio. Substituting in Equation (2),

$$\frac{n_x - n}{n_x} = \frac{P}{E}(1 - \sigma)\frac{p}{v} - \left(\frac{P\sigma}{E}\right)\frac{q}{v} = \frac{P}{E}\left[(1 - \sigma)\frac{p}{v} - \sigma\frac{q}{v}\right]. \tag{3A}$$

Similarly it can be shown that

$$\frac{n_y - n}{n_y} = \frac{P}{E}\left(-2\sigma\frac{p}{v} + \frac{q}{v}\right) \tag{3B}$$

and

$$\frac{n_z - n}{n_z} = \frac{P}{E}\left[(1 - \sigma)\frac{p}{v} - \sigma\frac{q}{v}\right]. \tag{3C}$$

When the coefficients p and q have once been determined, these three equations may be used for calculating the effect of a thrust, P, in the direction OY (Fig. XVI. 14) on the three indices of refraction n_x, n_y, and n_z corresponding to light vibrating in the directions OX, OY, and OZ. The changes in refractive index for a given thrust, P, depend on the elasticity constants E and σ, and the coefficients $\frac{p}{v}$ and $\frac{q}{v}$ which are characteristic of the given material and can be determined experimentally. The change of n_x is the same as that of n_z (for a thrust along OY) so that no birefringence is observed for a ray of light passing through the block in the direction OY; but the velocity of a ray in the direction of the triple arrow (*i. e.*, along OX) depends on the direction of vibration, that is, n_y is different from n_z and $n_y - n_z$, by definition, is the birefringence.[79]

Since ordinarily n_x and n_y do not differ from n by more than one part

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[79] In the case of a uniaxial crystal, birefringence is usually expressed as $n_\epsilon - n_\omega$, which is identical with $n_y - n_z$, the direction Y being the direction of the optic axis.

in 1000, we may put, with a maximum error of a small fraction of one per cent,

$$\frac{n_y - n}{n_y} - \frac{n_z - n}{n_z} = \frac{n_y - n_z}{n}$$

and therefore by subtracting Equations (3B) and (3C) we obtain

$$\frac{n_y - n_z}{n} = \frac{P}{E}(1+\sigma)\frac{q}{v} - \frac{p}{v}. \tag{4}$$

This equation may be put in slightly different form by making use of the identity

$$R = \frac{E}{2(1+\sigma)},$$

R being the modulus of rigidity. Substituting the value of *R* in Equation (4), we have

$$\frac{n_y - n_z}{n} = \frac{P}{2R}\left(\frac{q}{v} - \frac{p}{v}\right). \tag{5}$$

From Equations (4) and (5) it is evident that the birefringence is proportional to the difference of the two coefficients *p* and *q*. Conversely, *p* and *q* can not be determined by measurements of birefringence alone, but if in addition to the birefringence we measure the absolute retardation of a ray of light vibrating, say, in the direction *OY*, both *p* and *q* will be uniquely determined.

Suppose now that instead of a thrust we apply to the block of glass a hydrostatic pressure, *P′*. In order to obtain a relation connecting the coefficients *p* and *q* with the hydrostatic pressure *P′*, it is obvious from considerations of symmetry that it is sufficient to add the three equations, (3A), (3B), and (3C). Then since $\frac{n - n_x}{n_x}$ is approximately equal to $\frac{n - n_x}{n}$, we have

$$\frac{n_x - n}{n} = \frac{P'}{E}(2-4\sigma)\frac{p}{v} + \frac{P}{E}(1-2\sigma)\frac{q}{v} = \frac{P'}{E}(1-2\sigma)\left(\frac{2p}{v} + \frac{q}{v}\right) \tag{6}$$

By putting $\frac{E}{3(1-2\sigma)} = K$, in which *K* is the modulus of volume-elasticity,[80] the equation becomes

$$\frac{n_x - n}{n} = \frac{P}{3k}\left(\frac{2p}{v} + \frac{q}{v}\right) \tag{7}$$

which expresses in terms of known or measurable quantities the effect of hydrostatic pressure on the index of refraction, which of course under these conditions remains independent of the plane of polarization of the light.

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[80] $1/K = \beta$, the compressibility at constant temperature.

A mathematical discussion of the stresses developed in glass as a result of temperature gradients, and of the birefringence produced by the stresses, was given by Adams and Williamson.[81] This discussion is reproduced in Chapter XIV, in connection with the thermal endurance of glass.

Mueller[82] has discussed the theory of the photoelastic effect. The refraction in ordinary glass is due primarily to the oxygen atoms, which in SiO_2 glass contribute to the refraction 140 times as much as the silicon atoms. The Lorentz-Lorenz equation (cf. p. 388 for a test of the applicability of this equation to the specific refractivity of Na_2O-CaO-SiO_2 glasses) is assumed valid, since the distribution of oxygen atoms is entirely random in a glass. The birefringence is due to two causes. The first of these is the change in the lattice distances, which become greater between planes normal to the direction of a tension, but remain unaltered between planes perpendicular to the direction of strain. This produces in all cases a negative birefringence.* The second cause of birefringence is an atomic effect, resulting from the distortion of the outermost electrons of the oxygen atoms, which produces positive birefringence. In glasses having a low index of refraction, the atomic effect preponderates, but in the heaviest flints the lattice effect becomes dominant, and the photoelastic constant changes in sign.

Savur[83] measured the stress-optical coefficient in tension and in compression, with excellent agreement, and concluded that, within the limits of experimental error, and up to a stress of 100 bars, the law connecting double refraction and stress is accurately linear, and is the same for tension and for pressure.

Units

The effect of pressure on the refractive index is measured by the difference in refractive index of the two rays: n_ϵ, the extraordinary ray, polarized at right angles to the direction of thrust, and n_ω, the ordinary ray, polarized in the direction of the thrust, which is the optic axis. The two stress-optical coefficients are defined by the equations

$$n_z - n = B_2 P_y \text{ and } n_y - n = B_1 P_y,$$

in which n is the refractive index of the unstressed glass, n_z is the refractive index of the extraordinary ray, and n_y that of the ordinary ray, when the thrust P is applied in the direction of the y-axis. The relative

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[81] Adams, L. H., and Williamson, E. D., *J. Franklin Inst.*, **190**, 597, 835 (1920).

[82] Mueller, H., *Physics*, **6**, 179 (1935); *J. Am. Ceram. Soc.*, **21**, 27 (1938).

* Mueller defined $B = \frac{n_n - n_p}{P}$, in which n_n is the refractive index normal to the stress, n_p is that parallel to the stress; hence his B is opposite in sign to that defined above.

[83] Savur, S. R., *Phil. Mag.*, **50**, 453 (1925).

stress-optical coefficient, commonly called the stress-optical coefficient B, is the difference between B_2 and B_1;

$$B = (B_2 - B_1)\,P_y$$

Filon used the notation

$$C_1 = -B_2,\ C_2 = -B_1,\ C = B.$$

The dimensions of the unit $F^{-1}L^2$, are the reciprocal of those of a stress. The name "brewster" was proposed by Filon[84] for the unit of photoelasticity: 1 brewster = a relative retardation of one Ångstrom unit per mm. per bar = 10^{-7} $(n_\epsilon - n_\omega)$ per bar.

Experimental

The pioneer work of Brewster, who studied both the effect of pressure and of tension by putting a rectangular beam of glass under flexure, was confirmed by Fresnel.[85] Neumann[78] developed the mathematical theory of the subject. His conclusions were criticized by Kerr[86] and by Pockels,[87] who pointed out errors of calculation in Neumann's work. Wertheim[88] seems to have been the first to study glass under pure tension and pure pressure. Pockels[87] made a series of experiments on

TABLE XVI. 29—Effect of Pressure on the Optical Properties of Glass: the Stress-Optical Coefficient*

After Adams and Williamson (AW) *and Pockels* (P)

Table and No.	Observer	Type	B	p/v	q/v
VI.1.1	(AW)	516/620	−2.79		
.2	(AW)	523/590	−2.52		
.3	(AW)	573/420	−3.13		
.4	(AW)	574/570	−2.75		
.5	(AW)	606/440	−3.03		
.6	(AW)	608/570	−2.10		
.7	(AW)	616/370	−3.06		
.8	(AW)	655/330	−2.61		
.9	(AW)	756/270	−1.19		
III.4.19	(P)	545/503	−3.70	0.289	0.182
.25	(P)	571/430	−2.87	0.306	0.213
.40	(P)	645/341	−2.56	0.335	0.264
.43	(P)	751/276	−1.30	0.354	0.319
.47	(P)	963/197	+1.88	0.427	0.466
.48	(P)	507/614	−4.23	0.274	0.166
O428†	(P)		−2.70	0.269	0.147

* Values of $B = \frac{n}{2R}\left(\frac{q}{v} - \frac{p}{v}\right)$, in which n = refractive index, R = rigidity, p/v and q/v, optical coefficients. Unit: 1 Brewster = 10^{-13} bar.

†O428 same as III. 4 No. 6 except 2% Al_2O_3 in place of 2% ZnO.

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[84] Filon, L. N. G., *Proc. Roy. Soc. (London)*, **89**, 587 (1913).

[85] Fresnel, L., *Ann. chim. Phys.*

[86] Kerr, J., *Phil. Mag.*, **26**, 321 (1888).

[87] Pockels, F., *Ann. Physik*, *(4)*, **7**, 745 (1902).

[88] Wertheim, G., *Ann. chim. phys.* *(3)*, **40**, 156 (1854).

the effect of strain on a series of Schott glasses whose batch compositions were known. His results are given in Table XVI. 29. In the first paper, his glass O428 was identified erroneously with VS428 (No. 52 Table III. 4); the correct value of the physical properties and compositions given in Table XVI. 29 was obtained from later papers.[89] He found that in the flint glasses the effect diminished regularly with the content of PbO. The birefringence, $(n_\epsilon - n_\omega)$, ordinarily was negative, but for the heaviest glass studied, the birefringence had become positive. Pockels concluded that it would be zero for a glass of the composition SiO_2, 22.8; K_2O, 1.5; PbO, 75.7, and an attempt was made to make a glass of this composition. The resulting glass, an analysis of which gave: SiO_2, 23.64; Na_2O, 0.24; K_2O, 0.37; CaO, 0.34; PbO, 74.61; $Al_2O_3 + Fe_2O_3$, 0.80, was not of high quality, and showed a positive birefringence of about one-tenth that of the heavier glass. Pockels concluded that a diminution of 0.6 per cent in the PbO content would have caused the birefringence to vanish.

TABLE XVI. 30A—Values of Stress-Optical Coefficients Determined by Filon and His Associates*

	Observer and date				
Glass	Filon 1903	Filon 1907	Jessup 1920	Harris 1923	Savur 1925
3413A		3.36		3.66	
3413B		3.50		3.74	
3296B		3.17		3.36	
3749		2.47		2.70	
3453A		2.38		2.66	
2453B		2.35		2.66	
2783A		2.15		3.00	
2783B		2.46		2.92	
O154	2.87		3.01	2.96	
O152	2.74		2.95	2.76	
O103	2.84			2.96	
O41	1.78		1.84	1.83	
6652		Filon		2.18	2.29
4840		1910		1.42	1.38
O935		3.29			
UV3199		3.06			
UV3492					3.58
7641($\lambda = 5893$)					2.70
1809($\lambda = 5893$)					3.62

* Unit: 1 Brewster = 10^{-13} bar. Compositions are given below.

Adams and Williamson,[90] in connection with their exhaustive study of the annealing of glass, determined the relation between birefringence and stress for a number of glasses whose batch compositions were known. Their results are given in Table XVI. 29.

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[89] Pockels, F., *Ann. Physik*, **9**, 220 (1902); **11**, 651 (1903).

[90] Adams, L. H., and Williamson, E. D., *J. Wash. Acad. Sci.*, **9**, 609 (1919); *J. Franklin Inst.*, **190**, 597, 835 (1920).

Filon[91] and his associates Jessop,[92] Harris,[93] and Savur[83] measured several glasses, included in Table XVI. 30A; and studied the effect of frequency, temperature and time on the stress-optical coefficient.

Twyman and Perry[94] determined the change in index for both ordinary and extraordinary rays for a glass of composition: SiO_2, 54.83; Na_2O, 6.23; K_2O, 4.30; PbO, 34.64; $n_D = 1.5759$, $\nu = 41.3$; and found C_ω to be -5.81, $C_\epsilon = -2.32$.

It was shown by Kerr and by Pockels that the change in the absolute index of refraction as the result of uniform, hydrostatic pressure was of the same order of magnitude as the birefringence; and Adams and Williamson[95] calculated the effect for a light flint glass, No. 3 of Table VI. 1. For a hydrostatic pressure of 980 megabars, the index of refraction is increased 0.0012; this change of index is independent of the plane of polarization of the light. For a unidirectional thrust of the same magnitude, the refractive index of the glass is changed 0.00049 for the ray vibrating perpendicular to the axis of pressure, and 0.00020 for the ray vibrating in the direction of the thrust.

TABLE XVI. 30B—Compositions of the Glasses in Table XVI. 30A

Glass	Lit. Ref.	SiO_2	B_2O_3	Na_2O	K_2O	CaO	MgO	PbO	Al_2O_3
3413A, B	1	31.6	33.0		3.8			23.6	8.0
3296B	1	67.5	15.4		16.7		0.4		
3749A	1	70.2	5.9		23.9				
3453A	1	68.1	5.7		20.8		5.4		
2783 (*a*)	1	52.7	1.4		12.5			31.6	0.6
6652	2	41		1.4	3.8	0.7		51.3	0.7
4840	2	30.4		1.85	1.65	1.8		64.4	0.2
1908	1	35.4	34.3		7.4		0.5	18.7	3.7
O935	1	32.5	27.7		3.1			28.2	8.5
O152	3	Probably near No. 16, Table III. 4							
O154	3	Probably near No. 25a, Table III. 4							
O103	3	Probably near No. 37, Table III. 4							
O192	3	Probably near No. 41, Table III. 4							
O41	3	Probably near No. 42, Table III. 4							

a Also contains ZnO, 1.2.

1. Filon, L. N. G., *Trans. Roy. Soc. (London), A*, **207**, 263 (1908). Analyses by Rees, W. J.
2. Harris, F. C., *Proc. Roy. Soc. (London), A*, **106**, 718 (1924). Analyses by Spilhaus, K. W.
3. Filon, L. N. G., and Jessop, H. T., *Trans. Roy. Soc. (London), A*, **223**, 89 (1922).

Wertheim concluded that the birefringence produced by strain was independent of the wave-length of the light, that is, that there is no dispersion; but subsequent experiments showed this not to be true in general. Pockels[96] determined the birefringence for sodium, lithium

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[91] Filon, L. N. G., *Proc. Cambridge Phil. Soc.*, **11**, 478 (1902); *ibid*, **12**, 55, 313 (1902-4).

[92] Jessop, H. T., *Trans. Roy. Soc. (London), A*, **223**, 89 (1922). Filon, L. N. G., and Jessop, H. T., *Proc. Roy. Soc. (London), A*, **101**, 165 (1922).

[93] Harris, F. C., *Proc. Roy. Soc. (London), A*, **106**, 718 (1924). Filon, L. N. G., and Harris, F. C., *Proc. Roy. Soc. (London), A*, **130**, 410 (1931).

[94] Twyman, F., and Perry, J. W., *Proc. Phys. Soc. (London)*, **34**, 151 (1922).

[95] Adams, L. H., and Williamson, E. D., *J. Wash. Acad. Sci.*, **9**, 609, 622 (1919).

[96] Pockels, F., *Ann. Physik*, **11**, 651 (1903).

and thallium light, and found a distinct change in birefringence for the lighter glasses, but for the heavier glasses it was very small. Filon[91] made extensive studies on the variation with wave-length of the double refraction in strained glass, and concluded that the birefringence is greater in the violet than in the red for those light glasses that are not borates, and that the dispersion of birefringence would become zero at about 66 per cent PbO. In some light glasses, the change in birefringence with wave-length was found to be almost linear, but with heavier glasses it became parabolic, the difference of the refractive indices increasing much more rapidly toward the violet than toward the red. Savur[83] found the stress-optical coefficient to increase numerically from the violet toward the red, for a glass (Table XVI. 30A) containing about 64.4 per cent PbO; and the dispersion was sensibly nil for a glass (Table XVI. 30A) containing 51.3 per cent PbO. The apparent lack of agreement with Filon may have been due to the difference in the light used; Filon used the dispersion green-red, and Savur, yellow-indigo.

Filon[97] and Harris[98] studied the effect of increase in temperature on the birefringence produced by strain; the results of Harris are given in Table XVI. 31. The effect of strain in producing birefringence increased with the temperature in all cases except the first (Table XVI. 30B), and the abnormal behavior of this glass was ascribed to its comparatively high content of PbO. The glasses studied by Harris had been studied in 1912 by Filon who found smaller values for the stress-optical coefficient. It was suggested that the molecular condition of the glass changed rapidly when first manufactured, later settling down to a steady state; but the significance of these experiments is doubtful.

TABLE XVI. 31—Effect of Increase in Temperature on Birefringence Produced by a Stress* of Megabar, x10^{-7}

After Harris

Glass	16-18° C.	100° C.	200° C.	250° C.	300° C.	350° C.	400° C.
6652	2.18	2.22	2.30	2.39	2.43	2.56	2.58
4840	1.42	1.38	1.36		1.38	1.40	1.29
3413A	3.66	3.62	3.66	3.68	3.72	3.72	4.00
3413B	3.73	3.59	3.71	3.75	3.78	3.80	3.85
3296B	3.36	3.36	3.41	3.42	3.45	3.46	3.49

* Compositions in Table XVI. 30B.

ABSORPTION AND TRANSMISSION

When the absorption of light in glass is fairly uniformly distributed throughout the visible spectrum, and the amount of absorption is small,

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[97] Filon, L. N. G., *Proc. Roy. Soc. (London), A*, **89**, 587 (1913).

[98] Harris, F. C., *ibid, A*, **106**, 718 (1924).

the glass appears colorless and limpid; when the amount of uniform absorption increases, the glass takes on a greyish hue. When the absorption is significantly greater for light of any color, the transmitted light will appear of a complementary color; since the absorption is never sharp, the color will depend on the thickness of the sample. Comparisons are best made by means of curves showing the change of absorption or transmission with wave-length for samples of standard thickness.

The use of coloring oxides in glass is old, and the earliest glasses were usually colored. Neumann[99] has shown that copper oxide, modified by the presence of oxides of iron and manganese (Table I. 1), was the usual colorant in the ancient Egyptian glasses. Neumann found cobalt oxide in a lapis lazuli glass from Nippur, dated about 1400 B. C., the only example of cobalt oxide in antique glass.

Colorless Glass

The transmission of the usual "colorless" or "white" glass is limited chiefly by absorption bands in the infra-red and ultra-violet, as is indicated by their dispersion curves. The limits of transmission in the ultra-violet are determined largely by the content of Fe_2O_3, which appears to have an absorption in the near ultra-violet. The limit of transmission in the infra-red is determined largely by the content of FeO, which shows strong absorption at about one mμ. The effect of FeO is shown in the absorption curve of "Aklo" heat-absorbing glass, Fig. XVI. 15.

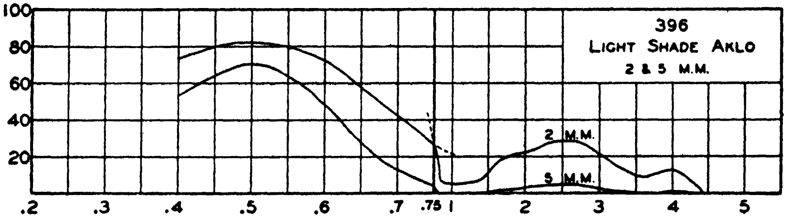

FIGURE XVI. 15.—Transmission Curve of Aklo Glass. Courtesy of Corning Glass Works.

"Vitreous silica,[15] in thicknesses such as are used in cameras and optical instruments, transmits all the radiation which acts vigorously on ordinary commercial photographic plates, that is, down to a wave-length of 220 mμ, but wave-lengths of 193 mμ and less are almost completely absorbed."

A silica-free glass which has a high transparency in the ultra-violet is Corex A, the transmission curve of which is shown in Fig. XVI. 16;

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[99] Neumann, B., and Kotyga, G., *Z. angew. Chem.*, **38**, 776, 857 (1925); Neumann, B., and Rupprecht, M., *ibid*, **40**, 963 (1927); Neumann, B., *Chem. Ztg.*, **51**, 1013 (1927); *Z. angew. Chem.*, **42**, 835 (1929).

and Fig. XVI. 17 shows the transmission curves of a series of glasses for controlling the ultra-violet part of the spectrum. Ordinary window glass removes the 313 mμ line and shorter wave-lengths.

The best optical glasses have a transparency of over 99 per cent throughout the visible spectrum, a result achieved only by the greatest care in excluding impurities, especially iron. Other optical glasses, especially those of higher index containing much lead or barium oxide, have a smaller transparency. Common window glass has a transparency of from 85 to 90 per cent. In recent years the quality of window glass has been greatly improved by the use of sand of low iron content, often making the use of decolorizers unnecessary. Such glasses have a transparency approaching that of optical glass, but when the color due to iron is masked by a decolorizer the transmission is reduced; and in some cases the glass is grey in thick pieces.

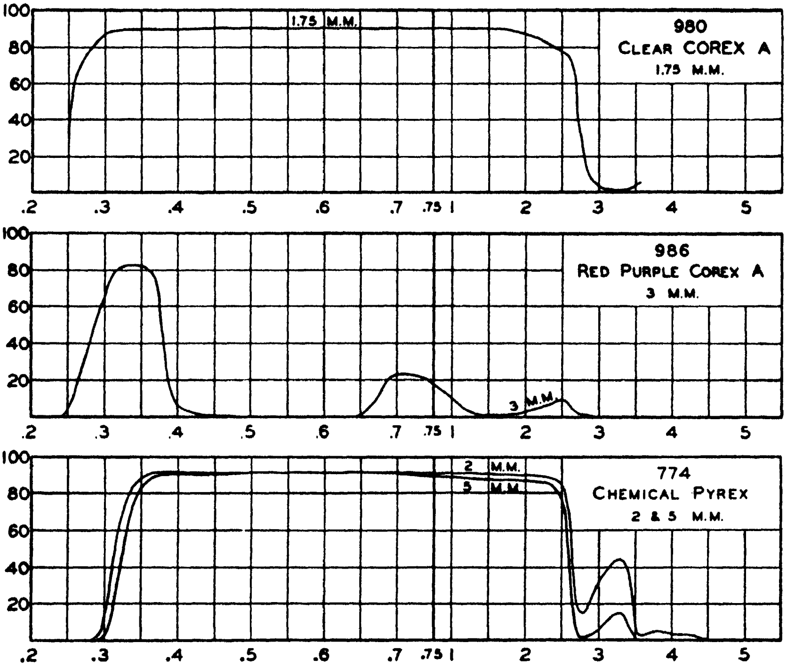

FIGURE XVI. 16.—Transmission Curves of Corex A Glass and of Pyrex Chemical Resistant Glass. Courtesy of Corning Glass Works.

Glasses transparent to x-rays are composed to the greatest possible extent of compounds of elements of low atomic number. "Lindemann glass" (p. 218) is highly transparent to x-rays, but difficult to make;

it cannot be shaped by blowing, and is rapidly attacked in the air. Schott[100] suggested a glass of the composition SiO_2, 39.6; B_2O_3, 30; Na_2O, 10; Al_2O_3, 20; As_2O_3, 0.4, for use as windows in x-ray apparatus.

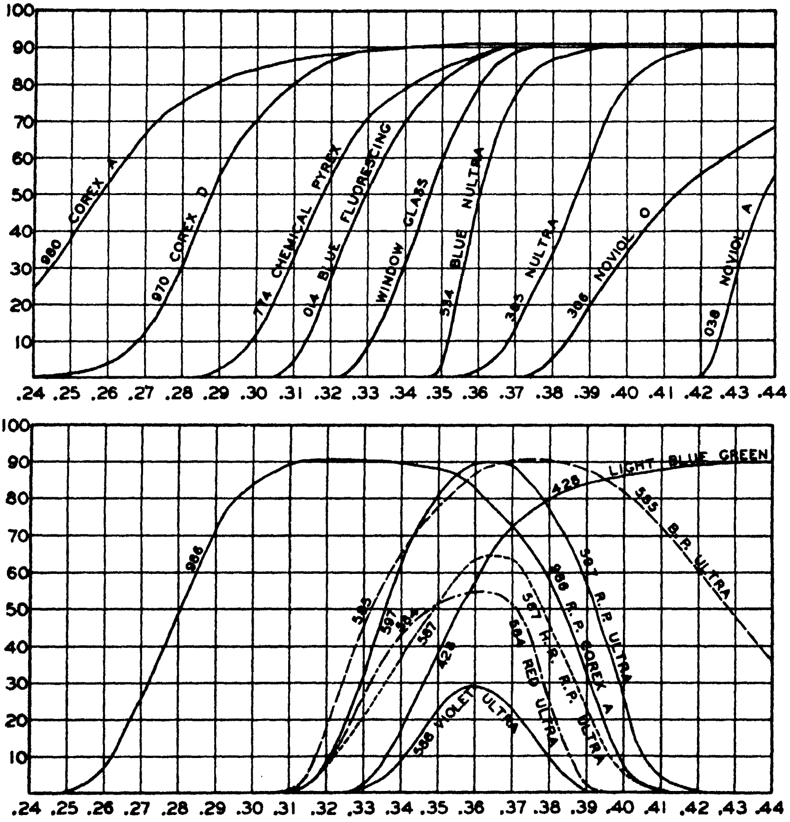

FIGURE XVI. 17.—Transmission Curves of Glasses for Controlling the Ultra-Violet Portion of the Spectrum. Courtesy of Corning Glass Works.

Colored Glasses

The coloring agent or colorant in glass usually is considered to be one of the following types: (1) the color is produced by absorption of characteristic frequencies by substances dissolved in the glass; (2) the color is produced by particles of sub-microscopic dimensions, colloidally dispersed in the glass; or (3) the color is produced by particles of microscopic or larger dimensions, either themselves colored, as in the aventurine glasses, or colorless, as in opal glass.

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[100] Schott, O., *Deut. Mech. Ztg.*, 13, 111 (1889).

The coloring agents which act by virtue of characteristic absorption spectra are all oxides of elements belonging to the transition groups of the periodic system, and especially to the first of these groups, in which the short periods having outer shells of eight electrons change to the longer periods having outer shells of eighteen electrons. To this group belong titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper, the commonest and most effective colorants of glass. From higher transition groups come the elements silver, uranium and the rare earths. Silver, which has weak tinctorial power, gives glass a yellow color, and is rarely used. Uranium is used chiefly for its fluorescent effect, sometimes for its tinctorial powers. The rare earths used as colorants give sharp absorption bands, in contrast to the broad bands given by most colorants.

The first systematic study of the effect of coloring oxides was that of Zsigmondy,[101] who worked in collaboration with Schott. Their studies showed the effect of most of the usual coloring oxides, and the effect of the base glass. Weyl and his collaborators [102] have added greatly to our knowledge of the mode of operation of the coloring oxides, and especially of the reasons for the wide range of colors obtainable with some colorants with change in the base glass, and on heat treatment. Norton [103] also has given a clear discussion of the action of the coloring oxides, as well as a comprehensive bibliography.

Weyl grouped the coloring oxides into those in which the variation in color is due to differences in the ionic environment in the glass, and those in which it is due to differences in oxidation. The state of oxidation of nickel oxide is not affected by melting under a large pressure of oxygen, yet the color obtained with nickel oxide may range from yellow to purple. The yellow color is due to the nickel oxide being saturated, that is, having associated with it the maximum number of nearest neighbors, corresponding to its maximum coördination number according to Werner's theory. This yellow color is obtained in lithium silicate glasses, in metaphosphoric acid glasses, and in glasses rich in boric oxide. When the glass is heated, or if the basic glass be a potash or rubidium glass, the saturated complex dissociates, giving rise to the color characteristic of the unsaturated complex, or to a mixture of the two colors. The unsaturated color obtained by dissociating a saturated complex by heat treatment often can be "frozen in" by rapid cooling. The effect of alkali oxide changes with atomic number; with lithium oxide the saturated complex can be obtained, with potassium or rubidium

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[101] Zsigmondy, R., *Ann. Physik.*, (*4*), 4, 60 (1901). Translation by Scholes, S. R., *Glass Ind.*, 10, 262 (1929).

[102] Weyl, W., *Glass Ind.*, 18, 73, 117, 167 (1937); *Glastech. Ber.*, 12, 641 (1931). Möttig, H., and Weyl, W., *Glastech. Ber.*, 11, 67 (1933). Weyl, W., and Thümen, E., *Glastech. Ber.*, 11, 113 (1933).

[103] Norton, F. H., *Glass Ind.*, 16, 45 (1935).

oxide, only the unsaturated; and with sodium oxide a mixture of the two.

The coloring action of cobalt is similar; the saturated color is red, the unsaturated is deep blue; and the color of a glass is determined by the proportions of the two complexes present. The red color may be obtained only in highly "acid" glasses, especially those rich in phosphoric or boric oxide; the usual blue color is obtained in more "basic" glasses, and is favored by high temperatures.

Other coloring oxides can be shown to exist in different states of oxidation. For example, Weyl and Thümen[104] found that by melting a glass of the composition $Na_2O \cdot 3SiO_2$ containing 0.1 per cent MnO at 1000° under increasing oxygen pressures the percentages of the manganese present as Mn_2O_3 could be changed as follows:

Oxygen pressure (atmospheres)	2	3	10	15	75	150	250
% Mn_2O_3	1	2	5	8	17	88	100

The purple color in manganese glasses is that of the trivalent manganese, which is usually present in small proportion but has intense coloring power.

Chromium oxide in glass gives colors ranging from pure green to yellowish green or orange, depending on the proportions of chromic oxide (Cr_2O_3) and chromate. The pure chromic oxide color can be obtained in melts of boric or phosphoric oxide, and in the presence of arsenic or antimony oxide. A pure chromate glass was made by Weyl by melting a sodium silicate glass and alkali chromate under 250 atmospheres of oxygen pressure. It was found that the characteristic absorption was in the ultra-violet, and that only a sharp absorption edge extended into the visible region. The equilibrium in glass is shifted toward the side of chromic oxide by increasing temperature, and is dependent on the composition of the base glass. "Acid" melts favor the chromic condition, "basic" melts the chromate condition; and potassium glasses behave more "basically" than soda glasses. Lead oxide and barium oxide stabilize the chromate condition.

Vanadium exists in glass as V_2O_3, which gives a green color, and as V_2O_5, which gives a brownish-yellow. Vanadium in the V_2O_5 condition has a strong absorption in the ultra-violet, which is useful in glasses for protecting the eyes. Because it is difficult to prevent its almost complete dissociation, vanadium is not used often as a colorant.

Of the rare-earth oxides, neodymium and praseodymium have the most pronounced coloring action; they are frequently used in their natural proportions as "didymium." Fig. XVI. 18 shows the typical spectrum of a didymium glass, with characteristic sharp absorption bands.

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[104] Weyl, W., and Thümen, E., *Glastech. Ber.*, 11, 113 (1933).

Uranium exists in glass as a mixture of uranous oxide UO_2, and uranate, UO_3. Under reducing conditions, the uranous oxide gives dark green glasses which are not technically important. They are used sometimes for color filters, and have typical band absorptions. The higher oxide, favored by oxidizing conditions, in basic glasses high in lead oxide gives a red color, the tomato red of lead uranate. In less basic glasses uranyl compounds are formed, which have a yellow color, and exhibit strong fluorescence. Uranium is used chiefly because of its fluorescent properties, especially for tubing for Neon lights.

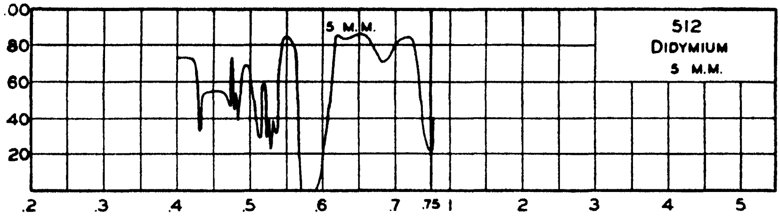

FIGURE XVI. 18.—Transmission Curve of a "Didymium" Glass. Courtesy of Corning Glass Works.

Copper in glass may be present both in the colorless cuprous condition, and in the strongly colored cupric condition. The color of the cupric oxide in glass is affected greatly by the base glass and by temperature, the two factors giving a color range from blue to green, intermediate between the cobalt and the chromium colors. When melted under reducing conditions the cupric oxide dissociates to the colorless cuprous condition, which can be retained when the glass is cooled. On reheating, however, cupric oxide and metallic copper are formed, and the copper may be obtained in colloidal condition, giving a "copper ruby" (p. 439). If much copper is present, or if it is strongly heated, flakes of metallic copper separate, giving the copper aventurine glasses.

Iron oxide is present in most glasses, and its color is usually objectionable. The ferrous glasses have a strong absorption in the near infra-red, giving a green or bluish-green color; the ferric glasses absorb in the near infra-red, giving a weaker yellow color which is less objectionable. Hostetter and Sosman [105] and Hostetter and Roberts [106] showed that ferric oxide is not stable under ordinary melting conditions, and dissociates into ferrous oxide and oxygen. The proportion of ferric iron is increased by the presence of arsenic or antimony oxide; they tend to give a yellowish-green under conditions which otherwise would give a blue-green. The green may be masked by the action of a "decolorizer," usually manganese

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[105] Hostetter, J. C., and Sosman, R. B., *J. Am. Chem. Soc.*, **38**, 1188 (1916).

[106] Hostetter, J. C., and Roberts, H. S., *J. Am. Ceram. Soc.*, **4**, 927 (1921).

or selenium, which produces a complementary color. The combined action of the iron and the decolorizer reduces the transmission, even to the extent of giving a grey color.

The composition of the base glass plays an important part with both types of colorants. With those oxides which exist in more than one state of oxidation, the proportion of the two oxides, as well as the intensity, position and width of the absorption band caused by the different states of oxidation, are affected by the perturbing effect of the fields of the surrounding atoms or atomic groups. With those oxides which exist in only one state of oxidation, this "association" effect is dominant. When more than one colorant is present, the interaction of the various factors causes the actual absorption effects produced to be too complex to be explained in simple terms or to be predicted with our present knowledge.

The glasses colored by colloidally suspended particles are among the most splendid known. Gold ruby, described by Neri,[107] was the first substance in which the nature of the colloidal state was elucidated by the ultramicroscope. It is produced by adding a small quantity of gold or gold salt to a glass batch, melting, and cooling. The cooled glass is colorless; the red color, developed by re-heating, is caused by an absorption maximum in the green. When more strongly heated, the particles increase in size and the color changes to blue. On prolonged heating, the gold particles coagulate and become coarser, and since gold has a maximum reflection in the yellow,[108] the color changes to brown. Because the color is so intense, the gold ruby usually is applied as a "flashed" coating on a colorless glass. Rooksby[109] was unable to demonstrate by means of x-rays the presence of metallic gold in an ordinary gold ruby, but was able to show its presence in a special glass containing 0.1 per cent gold. The best color is obtained in a heavy potash-lead base glass.

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[107] Neri, A., "L'Arte Vetraria," Florence, 1612. The following description has been copied from Merrett, C., "The Art of Glaſs, written in Italian by Antonio Neri, and tranſlated into Engliſh, with ſome Obſervations on the author," Chap. 129, p. 192, and p. 351, Octavian Pulleyn, London, 1662.

"Calcine Gold with Aqua-regis, many times, pouring the water upon it five or ſix times, then put this powder of Gold in earthen pans to calcine in the furnace till it becomes a red powder, which will be in many days, then this powder added in ſufficient quantity, and by little and little, to fine Cryſtall glaſs which hath been often caſt into water, will make the tranſparent red of a Rubie as by experience is found."

Merrett, in his "Obſervations on the Author," added:

"By conjecture hits right on this colour from Gold in theſe words. I judge that from a red tincture of Gold diſſolved into a liquor or oyl, and eſpecially with Cryſtall, a Rubie may not unfitly be made. Of which conjecture he aſſigns this reaſon, becauſe Rubies are frequent where Gold is found, and therefore 'tis conſentaneous that gold there doth degenerate into this jewel."

[108] Freundlich, H., "Colloid and Capillary Chemistry," translation by Hatfield, H. S., 800, Dutton, New York.

[109] Rooksby, H. P., *J. Soc. Glass Tech.*, **16**, 171 (1932).

Copper ruby is obtained in a similar manner by re-heating a colorless glass. The presence of zinc oxide is necessary, and the melting must be carried out in a neutral or reducing atmosphere. Rooksby has demonstrated by means of x-rays the presence of metallic copper in copper ruby.

Selenium dioxide, usually introduced as a selenite, is an important colorant. It produces a pink color; soda glasses have a yellowish tinge called salmon pink; potash glasses are rose or cerise. When used with cobalt oxide, it is an excellent decolorizer for masking the green tint of ferrous iron. When lead oxide is present, selenium gives a dark amber color.

Most of the ruby glass today is a selenium ruby, obtained by adding both selenium and cadmium sulfide and melting in a reducing atmosphere. The presence of zinc oxide is necessary. The resulting glass is a faint yellow, and the ruby color is brought out by re-heating. Rooksby[109] made an x-ray study of a number of selenium ruby glasses and found the coloration to be caused by the precipitation of particles composed of a solid solution of cadmium sulfide and cadmium selenide. Differences in the relative amounts of the two compounds in solid solution produced colors ranging from orange to deep ruby. The particles in the deep red glasses contained relatively more cadmium selenide than the orange glasses, and it was suggested that the color of the glass was due mainly to the color of the particles themselves rather than to their size and nature, as in the case of gold and copper ruby glasses. The work of Bigelow and Silverman[110] agreed with that of Rooksby. They found the batch yielding the best ruby to contain 2 per cent selenium, 1 per cent cadmium sulfide, 1 per cent arsenic trioxide, and 0.5 per cent carbon. Practical details of manufacture have been discussed also by Kirkpatrick and Roberts[111] and by Mathews.[112]

REFLECTION OF LIGHT

The proportion of light incident on a glass surface which is reflected depends on the frequency of the radiation, on the angle of incidence, on the refractive index of the surface and on the condition of the surface. The complete theory is complex, especially when the frequency approaches that of an absorption band; but for perpendicular incidence of light far removed from an absorption band, the proportion of light reflected is given by

$$R = \left(\frac{n-1}{n+1}\right)^2.$$

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[110] Bigelow, M. H., and Silverman, A., *J. Am. Ceram. Soc.*, **16**, 214 (1933).

[111] Kirkpatrick, F. A., and Roberts, G. F., *J. Amer. Ceram. Soc.*, **2**, 895 (1919).

[112] Mathews, W. J., *Ceram. Ind.*, **24**, 334 (1935).

This reflection results in loss of light, a loss which increases with the number of elements in the lens system and with the difference in refractive index of the two materials at the boundary surface.

It has been found[113] that treatment of a glass surface with certain chemicals reduces the loss by reflection by one-third to one-half. Ferguson and Wright found that the most effective treatment of a light flint glass ($n_D = 1.570$) was with a one per cent solution of acid sodium phosphate, acting for 18 hours at 80° C. Other solutions nearly equal in effectiveness were: phosphoric acid, one per cent solution; copper sulfate, two per cent; nickel sulfate, two per cent; ferric sulfate, two per cent with a little free sulfuric acid; potassium dichromate, two per cent. The change was so permanent that it did not disappear on ordinary rubbing or cleaning the surface, or after several years' exposure to the air. If the refractive indices of original and treated samples are measured by total reflection methods no difference can be detected. The reason for the effect is not known.

[113] Kollmorgen, F., *Trans. Illum. Eng. Soc. (N. Y.)*, **11**, 220 (1916). Wright, F. E., "The Manufacture of Optical Glass and of Optical Systems," *U. S. Ordnance Dept., Document No.* 2037; Govt. Printing Office, Washington, 1921.

Chapter XVII

The Electrical Conductivity of Glass*

Definitions and Units

The electrical conductivity of glass depends on the composition, on the temperature, and to some extent on the surrounding atmospheric conditions. At low temperatures, polycomponent glasses are insulators, and some are among the best insulating substances. At all temperatures, glasses are electrolytic conductors, and from 25° to 1200° C. the resistivity may range from 10^{19} ohms to 1 ohm.

The measurement of volume conductivity at low temperatures is complicated by the surface conductivity, which probably is caused by a layer of adsorbed moisture. The surface conductivity is particularly troublesome at high humidity and with glasses high in alkali and it may amount to many times the volume conductivity.

The volume resistivity is defined as the longitudinal resistance in ohms per unit of length of a uniform bar of unit sectional area; the volume conductivity is the reciprocal of the resistivity.

The surface resistivity is usually defined as the resistance in ohms of a strip of the surface of unit length and width.

Mechanism

Many studies of the conduction of electricity through glass have been undertaken to secure knowledge of the mechanism of this process. The early work of Buff[1] and of Beetz[2] was followed by the classic work of Warburg,[3] and its extension by Warburg and Tegetmeier.[4] Warburg established the basic fact of the electrolytic nature of the conductivity, which he found to take place in accordance with Faraday's law. He used test-tubes of Thuringian glass, filled with mercury or sodium amalgam and immersed in a similar bath, heated usually to 500° C. The mercury or amalgam inside and outside of the test-tube served as electrodes. With mercury electrodes, the conductivity rapidly

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* The discussion in the following pages is condensed from the monograph by Littleton, J. T., and Morey, G. W., "The Electrical Properties of Glass," John Wiley and Sons, New York, 1933; for a more extended treatment of some of the topics see that monograph.

[1] Buff, H., *Lieb. Ann.*, **110**, 257 (1859).

[2] Beetz, W., *Ann. Physik. Chem.* **Jubelband**, 23 (1874).

[3] Warburg, E., *Ann. Physik. Chem.*, **21**, 622 (1884).

[4] Warburg, E., and Tegetmeier, F., *Ann. Physik. Chem.*, **35**, 455 (1888).

diminished as electrolysis continued, falling to one-thousandth of its initial value in an hour. This decline was ascribed to the decrease in sodium content at the anode; this decrease was prevented by the use of sodium amalgam electrodes. With sodium amalgam electrodes, sodium was transported through the glass. Warburg and Tegetmeier showed that the conductivity of crystalline quartz is caused by the presence of sodium; later studies have failed to show whether the sodium is present as chloride, oxide or silicate, and the mechanism of the conduction[5] is still an open question.

Tegetmeier[6] found that, although the glass used by Warburg conducted with a sodium amalgam electrode, it did not do so with potassium amalgam. With lithium amalgam the glass conducted, with replacement of sodium by lithium, and formation of an opaque glass, which quickly shattered. Attempts to electrolyze with Ca, Mg, Al, Zn, Bi, and Au amalgam electrodes failed; the conductivity dropped immediately to zero, there was no transfer of metallic ions into the glass, and only a portion of the sodium ions in the glass took part in the conduction process. LeBanc and Kerschbaum[7] found that the glass could be restored to its original condition by electrolytic replacement of sodium in the anode layer, or by grinding off the anode layer. They also showed that when the anode layer was heated oxygen was evolved, in amount equivalent to the sodium evolved at the cathode. Mulligan, Ferguson, and Rebbeck[8] found that the anode gas can be obtained directly by electrolysis.

Roberts Austin[9] found that potassium could not be made to pass through glass, but that lithium could be, and ascribed the difference to the relative atomic volume of the lithium, sodium, and potassium ions. He also found that glass became colored by gold, dissolved either in a mercury or a lead anode. Heydweiller and Kopfermann[10] worked with closed tubes, immersed in a molten salt of the desired metal, or a molten mixture containing such a salt to serve as anode and a molten mixture of $NaNO_3$ and KNO_3 to serve as cathode. Current strengths ranged from 0.0005 to 0.25 ampere. They found that silver and copper gave colored dispersions of metal in glass, which changed color on heating, the silver especially having been marked by a change from yellow to intense red above 290°. Barium and strontium caused an increase in the current, and gave bubbly glass which broke on heating. Salts of tin, lead, cobalt and ferrous iron each caused the glass to become opaque and brittle, probably because the metals were present in a

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[5] See Joffe, A., "The Physics of Crystals," McGraw-Hill, New York, 1928.

[6] Tegetmeier, F., *Ann. Physik. Chem.*, **41**, 18 (1890).

[7] LeBlanc, M., and Kerschbaum, F., *Z. physik. Chem.*, **72**, 468 (1910).

[8] Mulligan, M. J., Ferguson, J. B., and Rebbeck, J. W., *J. Phys. Chem.*, **32**, 779 (1928).

[9] Austin, R., *Proc. Inst. Mech. Eng.*, **1895**, Pt. 1-2, 238.

[10] Heydweiller, A., and Kopfermann, F., *Ann. Physik*, **32**, 739 (1910).

colloidal condition. Gold, platinum and uranium apparently did not go into the glass.

An important improvement in the technique of studies on glass conductivity was that of Burt,[11] who used the thermionic emission from a heated metallic filament in an ordinary electric-light bulb to complete a direct-current circuit. The bulb was partially immersed in a bath of molten $NaNO_3$, and the Na ions discharged by the electrons from the filament condensed on the upper part of the bulb. Faraday's law was found to hold, and as much as 0.3 ampere could be passed through the bulb. Pyrex resistant glass was found not to be suitable for the bulb. With the soda glass, potassium ions from a KNO_3 bath did not pass through, but the current quickly dropped to a low value. Lithium ions did penetrate the soda glass, which became white, opaque and friable and would not hold a vacuum. Zworykin [12] found that potassium from molten KNO_3 did penetrate a soda glass, rendering it brittle, and did pass readily through a potassium glass without corroding the glass or rendering it brittle. Hurter [13] carried on similar experiments. Selényi [14] confirmed the work of the preceding observers, and also found that when the nitrate bath was made the cathode, the oxygen was electrolytically introduced within the bulb, in amount calculated from the quantity of electricity which had passed.

Hurd, Engel, and Vernon [15] studied the conductivity of glass in a similar manner, using solutions of NaCl, of $Na_2Cr_2O_7$, or of the fused eutectic mixture of $NaNO_3 + NaNO_2$, as an electrolytic bath. Metallic sodium was deposited inside the bulb, with no apparent effect on the glass, although at higher temperatures it became brownish. Heating the glass to redness in a flame was without result, and microscopic examination showed no cracking except in the vicinity of bubbles. Potassium ions, from solutions of KCl or from fused KCNS, penetrated easily, but any considerable depth of penetration resulted in fracture of the glass. No potassium could be detected spectroscopically in the sodium collected inside the bulb, but it was detected in a bulb of a special potassium glass. Even in this case, cracking resulted from an hour's electrolysis. The replacement of sodium by lithium ions, from a bath of fused $LiNO_3$, proved difficult, and the bulbs became opaque and cracked. The transfer of lithium could not be detected with ordinary glass before cracking, but could be detected with a special lithium glass, which, however, cracked after an hour's electrolysis. Ammonium ions could be transported through the bulbs, using saturated NH_4Cl solutions or fused NH_4NO_3, at 110°, without fracturing or discoloring the glass, unless the run was

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[11] Burt, R. C., *J. Optical Soc. Am.*, **11**, 87 (1925).
[12] Zworykin, V., *Phys. Rev.*, **27**, 813 (1926).
[13] Hurter, H., *Helv. Chim. Acta.*, **9**, 1069 (1926).
[14] Selényi, P., *Ann. Physik*, **84**, 111 (1927); **85**, 643 (1928).
[15] Hurd, C. B., Engel, E. W., and Vernon, A. A., *J. Am. Chem. Soc.*, **49**, 447 (1927).

continued for several hours. Heating always caused cracking, and at a dull red countless bubbles appeared along the cracks.

Details of the conduction process have been studied by Ferguson[16] and his co-workers. When a tube filled with mercury is electrolyzed by setting up a potential difference between the mercury and an external conductor such as a liquid electrolyte, gas is evolved at the mercury cathode. The gas was found to be a mixture of oxygen and hydrogen, but not in the proportions to form water. It was concluded that the gas is produced by the action of sodium on sorbed water and the simultaneous electrolysis of the sodium hydroxide produced. No gas was observed with glass in which the sodium had been replaced by silver, and on reversal of the current, the gas was largely resorbed. Anode gas could be obtained directly by electrolysis.

Kraus and Darby[17] made a careful study of the conduction process in glass and confirmed many of the earlier workers' conclusions. In addition, they made a quantitative study of the replacement of sodium by silver from a fused $AgNO_3$ bath, in a soda-lime-silica glass containing 16.90% Na_2O, 11.24% CaO (+ PbO), 2.35% ($Al_2O_3 + Fe_2O_3$). Faraday's law was found to hold accurately, and all the current was carried by the sodium ion. The depth of penetration of silver ions could be measured with a microscope, and hence the speed of the sodium ions calculated from the moving boundary. The results are given in Table XVII. 1, speed being measured in centimeters per volt per centimeter. From the composition of the glass the portion of the sodium present which takes part in the electrolysis, *i.e.*, the effective ionization, can be calculated. These results also are included in Table XVII. 1. It will be observed that the ionization increased appreciably over the temperature range studied, and it is considered probable that ionization is practically complete at temperatures around 1000° C.

TABLE XVII. 1.—Speed of Sodium Ions and Effective Ionization in a Soda-Lime-Silica Glass, at Various Temperatures

After Kraus and Darby

Temperature (° C.)	Speed	Ionization (%)
278	4.52×10^{-8}	76.5
295	1.46×10^{-7}	76.8
323	3.26×10^{-7}	77.05
343	5.9×10^{-6}	82.3

The purely electrolytic character of the conduction process in glass has been questioned by Poole[18] on the basis of some qualitative

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[16] Rebbeck, J. W., and Ferguson, J. B., *J. Am. Chem. Soc.*, **46**, 1991 (1924); Mulligan, M. J., Ferguson, J. B., and Rebbeck, J. W, *J. Phys. Chem.*, **32**, 779 (1928); *ibid.*, **32**, 843 (1928); Mulligan, M. J., and Ferguson, J. B., *Trans. Roy. Soc. Canada* (*3*), **21**, 263 (1927).

[17] Kraus, C. A., and Darby, E. H., *J. Am. Chem. Soc.*, **44**, 2783 (1922); Kraus, C. A., "The Properties of Electrically Conducting Systems," pp. 358, 359, New York, Chemical Catalog Co., (Reinhold Publishing Corp.) 1922.

[18] Poole, H. H., *Nature*, **107**, 584 (1921).

observations at ordinary temperature. In other experiments Poole[19] found a linear relation between the conductivity and the field strength, represented by the equation $\log K = A + BX$, where K is the conductivity in 10^{-12} reciprocal ohm per centimeter; and X, the potential gradient in megavolts per centimeter. Values of B decreased with the temperature, ranging from 1.50 at 14° to 0.91 at 74°. The influence of dielectric heating was not considered, and it is possible that this may account for the deviation from Ohm's law. Quittner,[20] using Schott Geräte glass and Schott 1447^{III} glass, at field strengths as high as 0.59×10^6 volts per centimeter, found the conductivity to be entirely electrolytic.

Kiehl[21] found that the current-voltage relationship depended largely on the previous history of the sample. With glass which had not been subjected to an electric field, Ohm's law held; but samples on which highly resistant layers had been formed gave characteristic irreversible absorption currents, and current voltage relations ranging from $I = AV^n$ to that of Poole. The highly resistant layer may have been the result of impregnation by the material of the electrodes.

Practically all investigators agree in ascribing all the conduction to the sodium ion, but it is probable that other conductivity effects are to be considered. There is great need for a more fundamental study of the conduction process in glass. At higher temperatures, all the current appears to be carried by the Na ion, but what is the part played by calcium in such a glass? If it is present as calcium ions, why does it not take part in the conduction? What would be the nature of the conductivity in an alkali-free glass such as wollastonite glass, $CaO \cdot SiO_2$? And how would the conductivity in this glass compare with that in a glass of the composition of the $CaO \cdot SiO_2$-SiO_2 eutectic? A thorough study of the conductivity of glass as a function of composition in the ternary system Na_2O-CaO-SiO_2, and at various temperatures, would be of the greatest value in extending our knowledge not only of the conductivity of glass, but also of the nature of glass itself. The ratio of the conductivity of strained glass to that of annealed glass is as much as three, a difference which is of a different order of magnitude from the effect of strain on other properties. The study of this effect may yield much information as to the constitution of glass.

Methods of Measurement of Electrical Conductivity

Because of the enormous change in electrical conductivity of glass with temperature, different methods are required in the various tempera-

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[19] Poole, H. H., *Phil. Mag.*, **42**, 488 (1921).

[20] Quittner, F., *Sitzber. Akad. Wiss. Wien*, **136**, 151 (1927).

[21] Kiehl, H. R., *Physics*, **5**, 363, 373 (1934); **7**, 20 (1936).

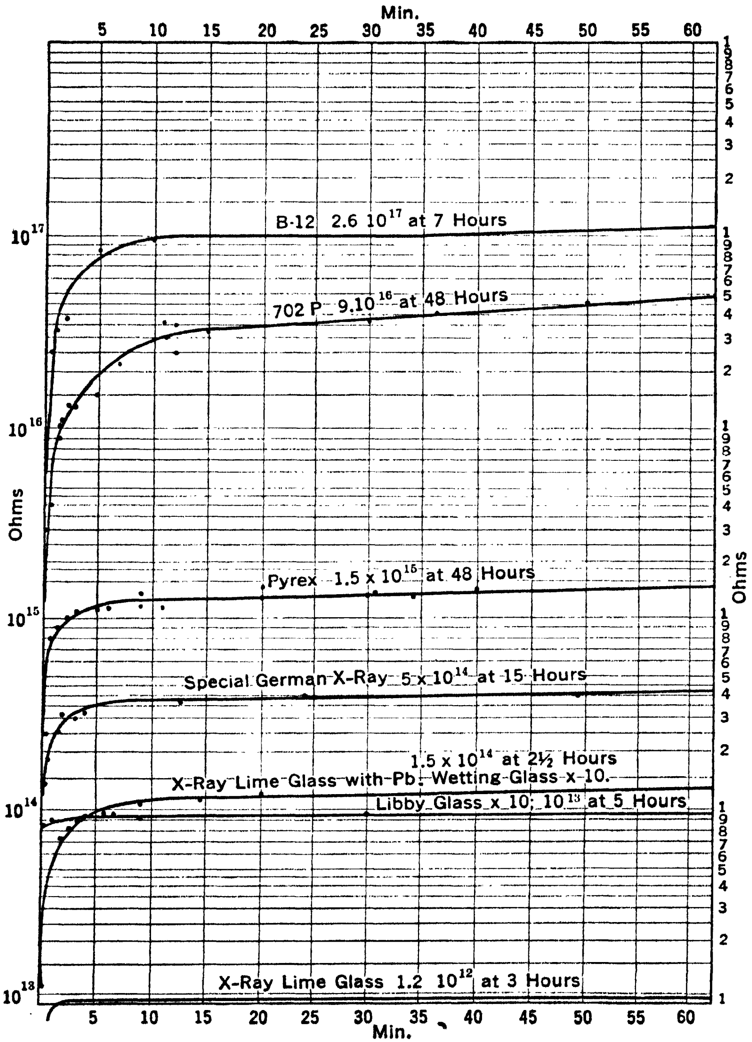

FIGURE XVII. 1.—Resistance of Dry Glass as a Function of the Time after Applying Voltage. After Bronson.

ture zones. Since the conductivity is electrolytic in character, the methods chosen must be such as to eliminate polarization, but this factor is not of importance at ordinary temperatures.

Curtis[22] gave the details of two methods used by him. For measuring resistances higher than 10^{15} ohms a Dolezalek quadrant electrometer

[22] Curtis, H. L., *Bull. Bur. Standards*, **11**, 359 (1914-15).

having a capacity of 130 micro-microfarads was used. By means of it resistances as high as 10^{17} ohms could be measured. For glasses having a lower resistance, a galvanometer method was satisfactory. In addition to these two standard methods for the measurement of very high resistances, a third method has been developed which makes use of a low grid-current Pliotron tube as a current indicator. No results for the resistivity of glass obtained with this apparatus have been published, but Rose[23] has given a complete description of the circuit.

In making measurements of high resistivities, due account must be taken of the absorption current, which may persist for hours. Curtis stated that immediately after applying the electromotive force the absorption current may be relatively large, but it decreases rapidly so that at the end of one minute the quantity absorbed per second is usually between 1/100 and 1/100,000 of the quantity which was displaced through

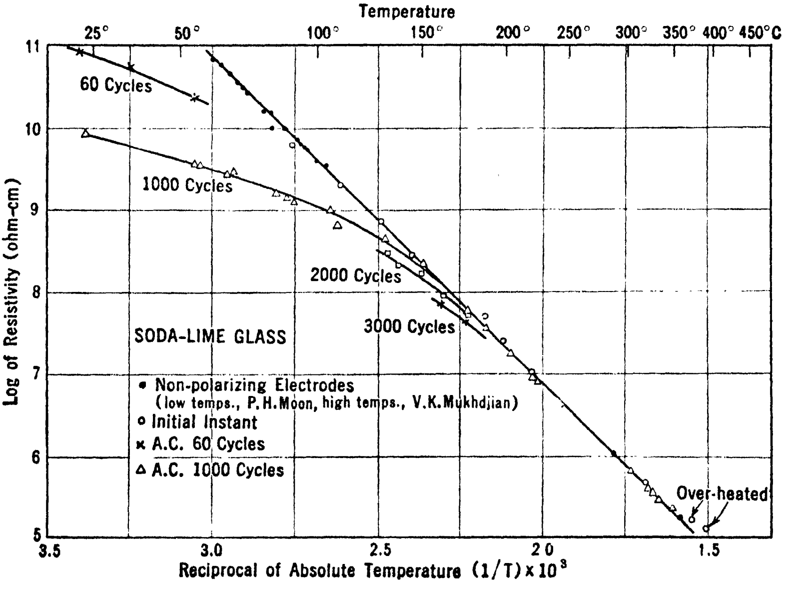

FIGURE XVII. 2.—The Resistivity of a Soda-Lime Glass as Measured by Various Methods. After Robinson.

the dielectric. In those cases in which the conductivity is less than about 10^{13} ohms, the absorption current gives no error greater than 10 per cent, provided the resistance is measured at the end of one minute. However, if the resistivity is above 10^{13} ohms, measurements must be made with different time intervals in order to determine when the

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[23] Rose, G. M., Jr., *Rev. Sci. Instruments,* **2,** 810 (1931).

absorption current becomes negligible. If the resistivity is greater than 10^{16} ohms, the absorption current at the end of one minute will probably equal the conduction current and may be much larger. Bronson,[24] studying leakage of insulators for "electrometer" tubes, found it necessary to polarize the glass by impressing the operating voltage for some hours before measurements were made. The need for this is shown in Fig. XVII. 1, which gives the resistance as a function of the time after voltage is applied. The apparent change in resistance which is due to the absorption current is enormous during the first ten minutes, and is still appreciable after an hour.

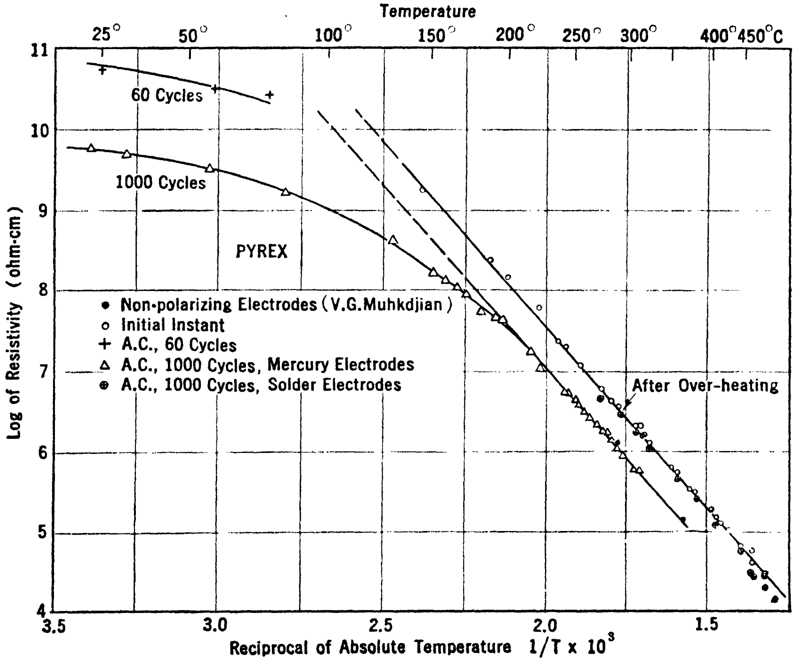

FIGURE XVII. 3.—The Resistivity of Pyrex Chemical Resistant Glass as Measured by Various Methods. After Robinson.

At temperatures above 100° the method used must be such as to prevent polarization of the electrodes. Robinson[25] compared several methods, namely, the use of non-polarizing electrodes, measurement of the instantaneous current, and the use of alternating current of various frequencies. The non-polarizing electrodes were baths of fused sodium nitrite or sodium thiosulfate, which by supplying the sodium ions pre-

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[24] Bronson, H. L., cited by Hull, A. W., *Physics*, 2, 420 (1932).

[25] Robinson, D. M., *Physics*, 2, 52 (1932).

vented the formation of a high-resistance surface layer. The slow rate of current decay made it possible to apply the voltage for a short known interval of time, $\frac{1}{8}$ second, and to measure the quantity of electricity passed by the sample with a ballistic galvanometer. The error so introduced was less than five per cent. The results with three types of glasses, namely, a soda-lime glass, a lead glass, and Pyrex resistant glass, are shown in Figs. XVII. 2, 3, 4. The samples were in the form of tubes 20 cm. long, sealed at one end, filled with the liquid electrolyte to about 2 cm. of the top and fixed within a larger tube also filled with the liquid electrolyte to the same height. Up to 250° C., mercury was used for both electrodes, and above that temperature, soft solder. The results with polarizing electrodes agreed very closely with those obtained with non-polarizing electrodes over the whole range over which they could be compared, namely, from 60° to 250° C., and the two direct-current methods gave a straight-line plot over the whole range from 20° to 520° C. Between 140° and 250° the resistivity as measured with alternating current agreed with direct-current values, but below 140° the alternating-current values became lower, indicating an additional

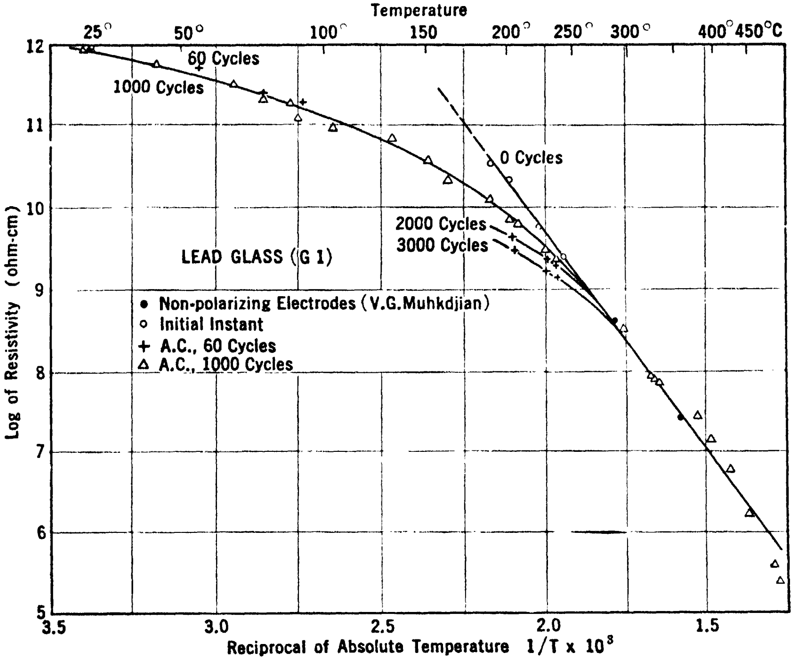

FIGURE XVII. 4.—The Resistivity of a Lead Glass as Measured by Various Methods. After Robinson.

component of loss. This effect increased remarkably with frequency, both between 60 and 1000 cycles and between 1000 and 3000 cycles. The higher the frequency the higher the temperature at which the additional loss was noticeable. Robinson pointed out that, although this loss could be explained either by the Debye theory of polar molecules or by the Wagner theory of imperfect dielectrics, the lack of evidence as to the existence of polar molecules in glass made the exact nature of the loss uncertain. No mention was made of the possible effect of dielectric heating in causing this difference, and sufficient data to estimate it were not given; but this effect may have accounted for a major part of the observed difference between direct- and alternating-current methods.

At temperatures near and above the annealing temperature, alternating-current methods alone are used. Sutton and Silverman [26] used a Vreeman oscillator, using a frequency of 1000 cycles, and platinum electrodes. Fulda [27] used a 60-cycle frequency and an electrodynamometer as a current measuring instrument. Bryson [28] introduced an improvement in technique consisting of the use of a vacuum tube as an alternating-current generator.

Conductivity at Low Temperatures

Surface conductivity. Since the time of Faraday,[29] it has been inferred that part of the conductivity of glass may be ascribed to a film of water condensed on its surface. The existence of such a film was demonstrated by Warburg and Ihmori,[30] who showed that near the dew-point this film reached a thickness of several millionths of a centimeter, that with the better glasses all the film was removed in a dry atmosphere, and that with inferior glasses all the film could be removed only by heating. The thickness of the adsorbed film on glass has been the subject of many studies, which have been summarized by several writers.[31] The problem is a difficult one, and there is no unanimity among the various investigators as to the thickness of the film, or indeed, if it is merely adsorbed film, or if there is in addition some absorption of water in the glass. It has been held that the film builds up until it becomes a monomolecular layer, at about 50 per cent humidity, which according to the calculations of Yager and Morgan [32] should be easily detected by its conductivity. It is problematical, however, whether the water arranges itself in an orderly manner over the surface of the glass. It is more prob-

[26] Sutton, W. J., and Silverman, A., *J. Am. Ceram. Soc.*, 7, 86 (1924).

[27] Fulda, M., *Sprechsaal*, 60, 769 (1927).

[28] Bryson, F. F. S., *J. Soc. Glass Tech.*, 11, 331 (1927).

[29] Faraday, M., *Trans. Roy. Soc. (London)*, 1830, part 1, 49.

[30] Warburg, E., and Ihmori, T., *Ann. Physik Chem.*, 27, 481 (1886).

[31] McHaffie, I. R., and Lenher, S., *J. Chem. Soc.*, 127, 1559 (1925); Frazer, J. C. W., Patrick, W. A., and Smith, H. E., *J. Phys. Chem.*, 31, 897 (1927); Stromberg, R., *Kgl. Svenska Vetenskapsakad. Handl.*, 6, 1 (1928).

[32] Yager, W. A., and Morgan, S. O., *J. Phys. Chem.*, 35, 2026 (1931).

able that certain spots representing a predominantly alkaline grouping will collect water in layers many molecules thick, while other spots will have no tendency toward absorption of water. There would then be no continuous layer until the water condensed by the alkaline spots spread out over the water-free areas. Moreover, the layer in question is not one of pure water, but rather is an aqueous alkaline solution of increasing strength, and hence of changing properties. Curtis[83] found the surface resistance to vary with the humidity, as shown in Figure XVII. 5. The compositions of the glasses were not determined, but the Kavalier glass probably did not differ significantly from No. 2, Table III. 3. When well cleaned before the experiment, fused silica glass gave a curve which

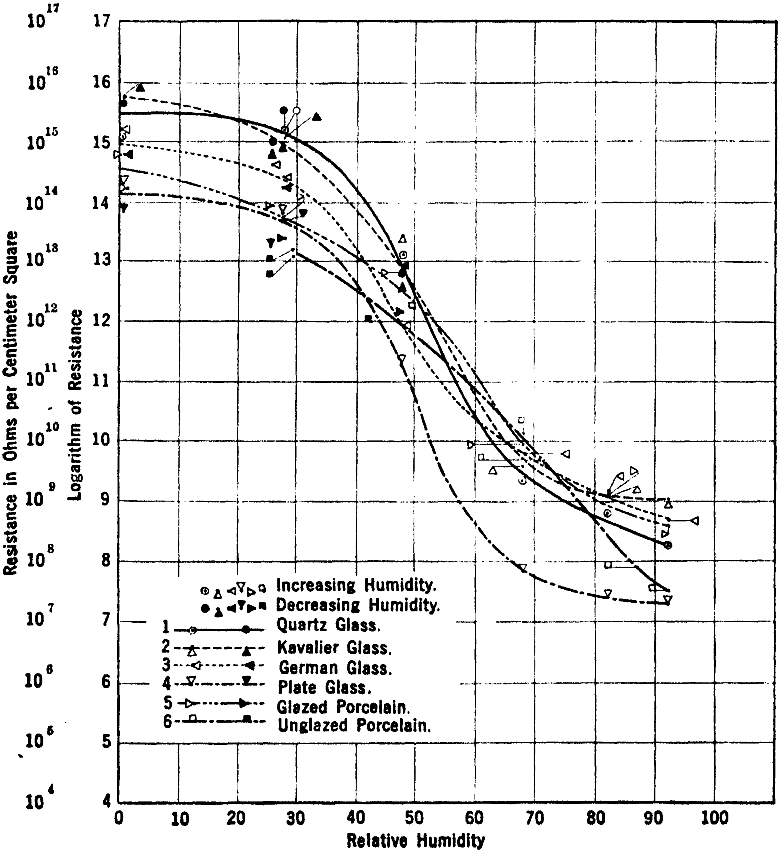

FIGURE XVII. 5.—The Change of Surface Resistivity with Humidity of Several Substances. After Curtis.

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[83] Curtis, H. L., *Bull. Bur. Standards*, **11**, 359 (1914-15).

was well above that for the untreated glass, which fell but slowly with increasing humidity, and which at 90 per cent still was greater than 10^{13} ohms. Curtis calculated that the conductivity of the film on untreated silica glass, assumed to be 6×10^{-6} mm. in thickness, would be accounted for by the presence of 6×10^{-9} gram NaCl. Cleaning reduced the conductivity of the better grades of glass, but did not improve that of the poorer grades.

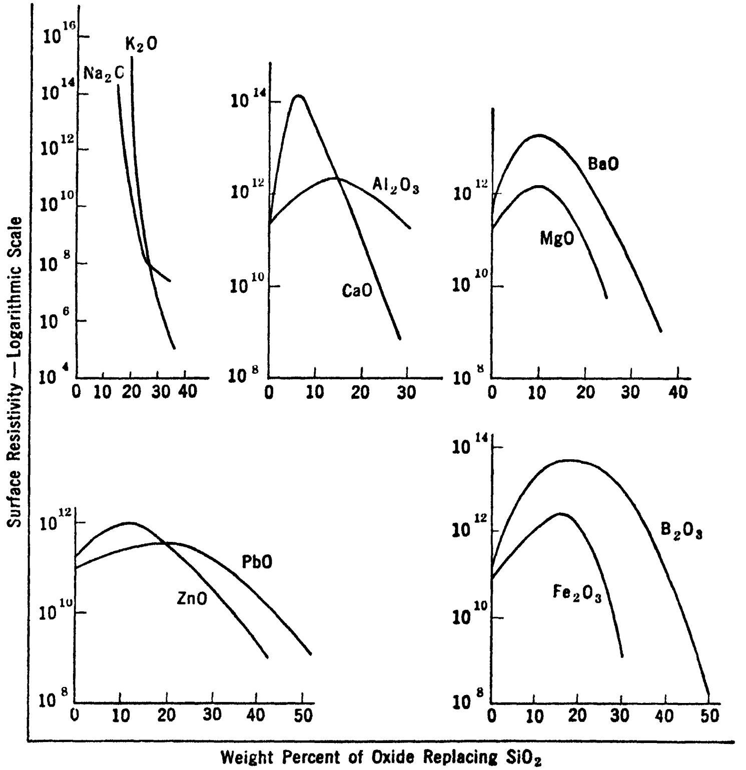

FIGURE XVII. 6.—The Effect on Surface Resistivity at 25° C., 100 Per Cent Humidity, of Replacing SiO_2 in the Glass $0.18Na_2O$, $0.82SiO_2$ by the Indicated Percentage by Weight of Other Oxides. After Fulda.

The most extensive study of the surface conductivity was that of Fulda,[34] who used the series of glasses studied at higher temperatures by Gehlhoff and Thomas.[35] The measurements were made in connection with a study of volume conductivity. The glasses were heated at 300° to 400°, cooled to 25°, and the conductivity determined, after which

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[34] Fulda, M., *Sprechsaal*, **60**, 769, 789, 810, 831, 653 (1927).

[35] Gehlhoff, G., and Thomas, M., *Z. tech. Physik*, **6**, 544-54 (1925).

water-saturated air was drawn over the surface for 15 minutes and the conductivity again determined. The difference between the two conductivity measurements was taken as the conductivity of the surface. The thickness of the surface layer was arbitrarily called unity, and the specific conductivity of a cylinder of length l and diameter d calculated from the formula: $w_s = wl/d$, in which w_s and w are the specific conductivity and measured conductivity, respectively. The results, expressed as specific resistances, are shown in Fig. XVII. 6. The curves "K_2O" and "Na_2O" refer to replacement of SiO_2 by K_2O or Na_2O, in a glass of the initial composition 0.20 PbO, 0.80 SiO_2. An increase in the alkali content resulted in an immediate and rapid decrease in the surface resistivity. Up to 30 per cent K_2O the potash glasses were the more resistant, but on further increase in the alkali content, the soda glasses diminished in resistivity less rapidly than before and became superior to the potash glasses. All the other curves refer to the progressive substitution for SiO_2 of the indicated oxide in a glass of the initial composition 0.18 Na_2O, 0.82 SiO_2. Each of these replacements had an initial beneficial effect on the surface resistivity, which passed through a maximum, after which further substitution had a deleterious effect. The maxima were found at 6% CaO and Al_2O_3, 10% CaO and MgO, 12% ZnO, 16% Fe_2O_3, 20% B_2O_3, and 21% PbO. The figures refer only to replacements in the particular glass studied by Fulda, and do not necessarily have any bearing on similar replacements in a glass of any other initial composition in the binary system Na_2O-SiO_2, or still less in more complex glasses. Other studies, considered below, indicated that the time of 15 minutes allowed by Fulda for attainment of equilibrium was inadequate, and the figures are to be regarded as a measure of the speed of surface attack rather than as equilibrium values.

Yager and Morgan[36] made a special study of the surface conductivity of Pyrex resistant laboratory glass as affected by both the humidity and the frequency. Their results are represented by Fig. XVII. 7, in which the surface conductivity is plotted against the percentage of relative humidity at 25° and at 50° and for frequencies ranging from 1 to 100 kc. They found that with low humidities two hours was usually sufficient to obtain constant values, but at higher humidities much longer times were necessary. At 30 kc. and 25°, equilibrium was not attained in 20 hours, and at 50° and 95 per cent humidity it was impossible even to approach equilibrium. It should be emphasized that the results of Fulda are not comparable with those of Yager and Morgan, because of the failure of Fulda to secure equilibrium. Great care must be taken in comparing the surface properties as measured by different investigators to insure that the experimental conditions are comparable, a matter par-

[36] Yager, W. A., and Morgan, S. O., *J. Phys. Chem.*, **35**, 2026, 2040 (1931).

ticularly important when the property in question is determined by the rate of a chemical reaction, as is the case with surface conductivity.

Bronson,[37] working in the research laboratories of the General Electric Company, studied insulation leakage and found that the better commercial glasses are satisfactory insulators for the most sensitive "electrometer" tubes, provided the glass is clean and properly "polarized." Cleanliness is paramount. "Quartz insulators" (probably silica glass) mounted in vacuum, leak badly if they have been touched with the fingers before mounting. Fig. XVII. 8 gives the variation of resistance with temperature above ambient of some typical glasses and of "quartz" on a humid summer day. This shows that clean glass can be used without

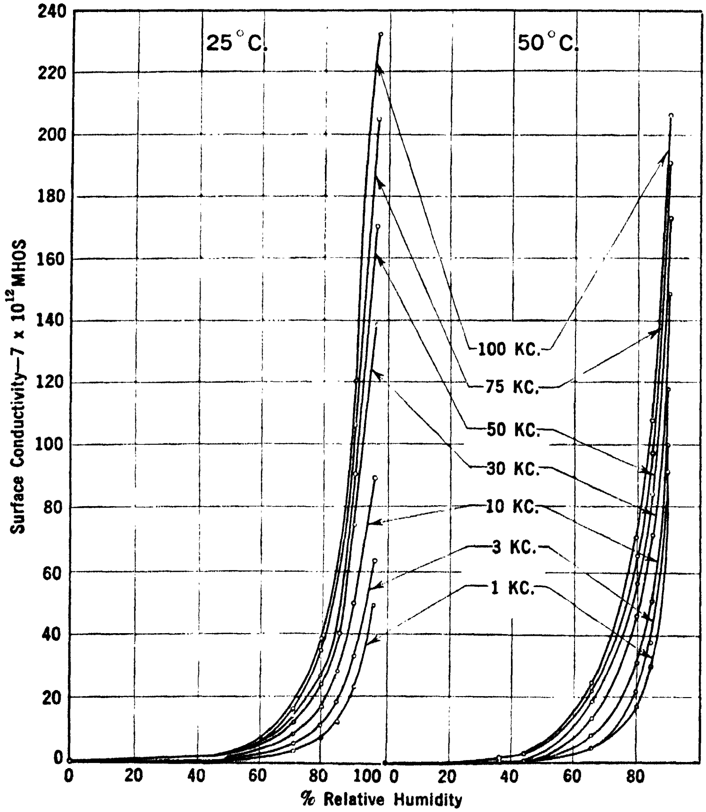

FIGURE XVII. 7.—The Surface Conductivity of Pyrex Chemical Resistant Glass at 25° C. and at 50° C. for Various Frequencies as a Function of Relative Humidity. After Yager and Morgan.

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[37] Bronson, H. L., cited by Hull, A. W., *Physics* 2, 409, 420 (1932).

serious leakage if the temperature is raised a few degrees above that of the surrounding air. The sample marked "Libbey" is a high-melting steam-gauge tubing; the immediate increase in conductivity indicates that the volume conductivity predominates over surface leakage. Corning 702P and Pyrex resistant glass showed optimum temperatures above ambient of 20° and 10° respectively for the particular form tested. The total resistivity of silica glass with its negligible volume leakage increased with increase in temperature. The results of such experiments, however, depend on the absolute magnitude of humidity, on ambient temperature, and on insulator shape.

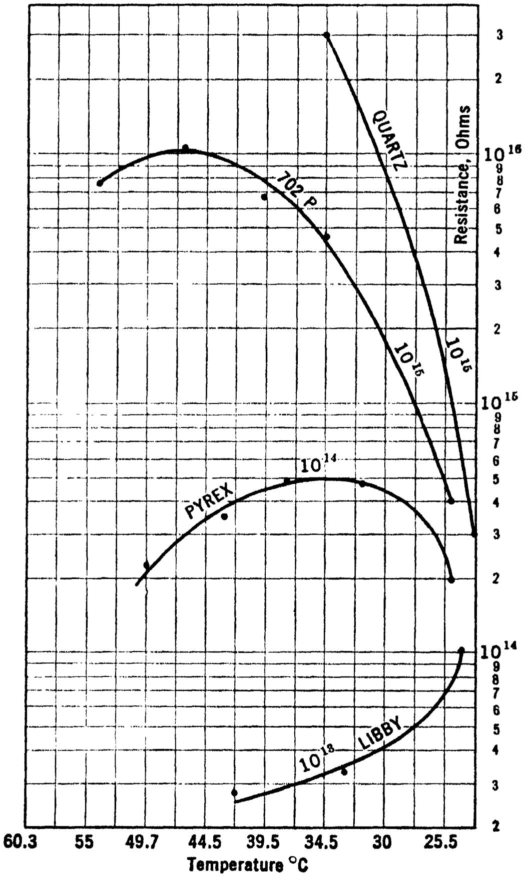

FIGURE XVII. 8.—The Variation of Resistance with Temperature above Ambient, on a Humid Summer Day. After Bronson.

Studies of surface conductivity agree in showing that in inferior glasses it may greatly exceed the volume conductivity, but that with the better grade of glasses, properly handled, it is entirely negligible. Proper handling includes absolute cleanliness, maintenance of a humidity well below saturation (better well below 50 per cent), and proper polarization. The measure of moisture content in the atmosphere is usually given as a percentage humidity, but it may be that the absolute moisture content would be a better measure. Carried out under proper conditions, the measurement of surface conductivity might be an excellent method of comparing the relative resistance of glasses to weathering.

TABLE XVII. 2—The Specific Resistance and Dielectric Constant of Glasses of Known Composition

After Gray and Dobbie

No.	Density	Temperature (° C.)	Specific Resistance Ohms $\times 10^{10}$	*K*	Composition							
					SiO_2	B_2O_3	Na_2O	K_2O	MgO	BaO	PbO	$Al_2O_3+Fe_2O_3$
21	3,495	15	....	7.966	50.5	...	Tr.	6.93	...	....	42.14	0.41
		130	18,000	7.630								
22	3.591	14	....	7.991	44.5	...	0.5	8.0	...	....	46.6	
		135	35,000									
23	3.565	135	59,000	8.5	33.0	12.0	Tr.	Tr.	...	48.0	MnO 1.0	6.0
24	3.493	15	....	7.54	67.6	8.0	10.0	....	5.0	ZnO 9.0	0.4	Tr.
		43	596.5									
		140	0.2									
25	2.487	11	....	6.26	69.04	...	19.23		CaO 7.59	....	1.31	2.73
		55	531.1									
		72	69.2									
		93	11.9									
		116	1.9									
		129	....	6.79								
		149	0.2									
26	2.99	10	....	7.06	58.83	...	7.35	6.42	MnO 0.81	....	PbO 26.10	0.43
		66	18,034									
		88	1,956.5									
		101	442.7									
		130	33.6	7.90								
		140	16.64									
		150	8.5									
27	3.552	8	....	5.42	40.79	...	13.76		...	....	45.19	0.29
		90	5,249									
		116	797.3									
		130	....	5.69								
		142	136.5									
28	3.11	22	....	6.93	52.28	...	0.64	19.74	...	26.09	....	0.25
		77	1,118.5									
		95	178.1									
		125	16.0									
		128	6.5									
		147	....	7.18								
29	3.41	18	Too high	7.22	48.25	...	....	10.65	...	....	40.80	0.29
		140	to measure	7.42								
30	3.34	18	....	6.76	50.11	...	....	10.03	...	....	39.74	0.12
		140	1,329	7.05								
31	3.408	20	....	8.013	50.42	...	8.77	....	...	....	40.24	0.38
		84	515.9									
		102	102.8									
		122	20.5									
		140	4.9	8.302								
32	3.36	19	....	7.376	51.46	...	9.13	....	...	Tr.	38.94	0.25
		73	215.1									
		83	144.6									
		104	20.8									
		120	4.9									
		130	....	8.44								
		140	1.7									

Volume Conductivity.

One of the first to demonstrate that glass itself has a real electrical conductivity was Ekman,[38] who studied the rate of dissipation of an electrical charge from a Leyden jar. Five glasses were compared as to their electrical and chemical stability, and it was found that, although two glasses inferior in chemical stability were also poor insulators, in another comparison the glass which showed inferior chemical stability was a superior insulator. He concluded that most of the charge was dissipated by conduction through the glass, and that Na_2O gives a conducting glass, K_2O a non-conducting glass.

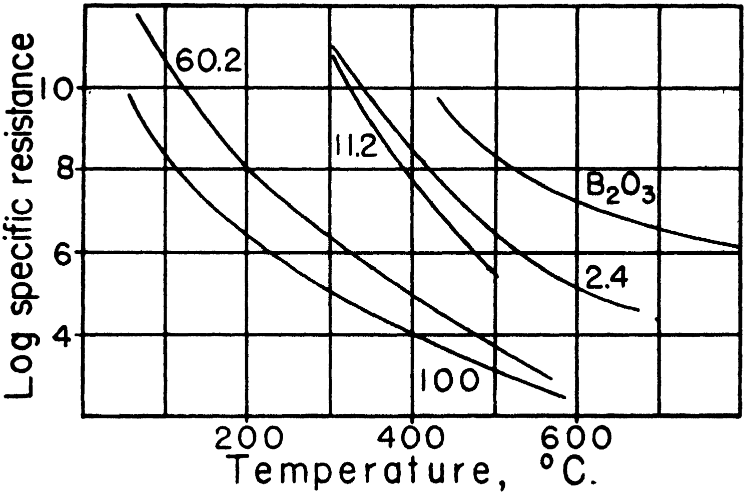

Figure XVII. 9.—The Specific Resistance of Several Boric Oxide-Sodium Diborate Glasses, containing the indicated Percentages of Sodium Diborate, $Na_2O \cdot 2B_2O_3$. After Thomas.

T. Gray [39] and A. Gray and Dobbie [40] measured the variation of resistance with temperature up to 140° of a number of glasses summarized in Table XVII. 2. They concluded that a substitution of potassium or barium for sodium in a glass of complex composition increases the resistivity, and also that a glass approaching a definite compound in composition has a high resistance. This last conclusion is fallacious: the evidence, for example, is that glass (21) which is capable of being expressed by a "simple" chemical formula, $2K_2O \cdot 5PbO \cdot 22SiO_2$, has a high resistivity, but no evidence is presented that such a compound

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[38] Ekman, F. L., *Phil. Mag.*, **4**, 39 (1870).

[39] Gray, T., *Proc. Roy. Soc.* (*London*), **34**, 199-208 (1882); Gray, T., Gray, A., and Dobbie, J. J., *Proc. Roy. Soc.* (*London*), **36**, 488 (1884).

[40] Gray, A., and Dobbie, J. J., *Proc. Roy. Soc.* (*London*), **63**, 38 (1898); **67**, 197-207 (1900).

exists. The mere chance that a glass composition can be approximately represented by a more or less complex formula has no bearing on the existence of a compound represented by that formula.

Curtis[41] found the volume resistivity of fused silica in ohm-centimeters at 22° C. to be over 5000×10^{15}; of Kavalier glass (probably near to No. 3, Table III. 3), 8×10^{15} of plate glass, 20×10^{12}; of opal glass, 1×10^{12}. He also found a slight change in resistivity with applied emf, $R_{50V}/R_{500V} = 0.7$, and the ratio of resistivities at 30° and 20° to range from 2.5 to 4.5.

Thomas[42] measured the conductivity of some glasses in the system Na_2O-B_2O_3, using the a.-c. bridge method up to about two megohms, and the d.-c. ammeter-voltmeter method, with a high sensitivity galvanometer or ammeter, for higher resistances. The mixtures were made by heating "several hours at the full heat of a blast lamp." The results are given in Fig. XVII. 9. In the temperature range used, all the glasses containing Na_2O were below their liquidus.

McDowell and Begeman[43] measured the apparent resistivity at 20° of six glasses: two lead glasses of unknown composition, Nos. 1 and 3; three borosilicates not containing any heavy metals, Nos. 2, 4, and 5, of which No. 2 was Pyrex chemical resistant glass; and No. 6, a lead borosilicate. The resistivity was measured after a brief unmeasured interval of time after the application of the potential difference, and therefore the results obtained are undoubtedly lower than the final resistivity. Following are the values found for specific resistivity at 20°:

Glass No.	Specific Resistivity
1	2.3×10^{13}
2	3.1×10^{14}
3	2.0×10^{15}
4	2.5×10^{15}
5	3.5×10^{16}
6	8.1×10^{19}

The extensive measurements of Fulda[44] have greatly increased our knowledge of the resistivity of glass as a function of composition. The glasses were heated at 300° to 400° C., cooled to 25° in a dry atmosphere, and measured. His scheme of variation of glass composition is explained on p. 326; the results are assembled in Fig. XVII. 10.

Replacing SiO_2 by Na_2O or K_2O in a glass containing 20 per cent PbO, 80 per cent SiO_2 results in a rapid decrease in resistivity, the potash glasses being the poorer conductors. Replacement of SiO_2 by Al_2O_3 also lowers the resistivity, although in a much less degree. All other replacements increase the resistivity, the effect being greatest with

[41] Curtis, H. L., *Bull. Bur. Standards*, 11, 359 (1914-15).

[42] Thomas, S. B., *J. Phys. Chem.*, 35, 2103 (1931).

[43] McDowell, L. S., and Begeman, H., *Phys. Rev.*, 31, 476 (1928).

[44] Fulda, M., *Sprechsaal*, 62, 769, 789, 810, 831, 653 (1927).

CaO and least with ZnO. The curves for BaO and PbO pass through well-marked maxima, and it is probable that some of the other curves would show a similar behavior if sufficiently prolonged. It must be remembered that these curves represent but an arbitrary excursion into the three-component system along one straight line, and it is not to be inferred that a curve of similar shape would result from an excursion along another straight line, or with an initial glass of any other composition. The inclusion of an additional component will affect the curves in an unpredictable manner.

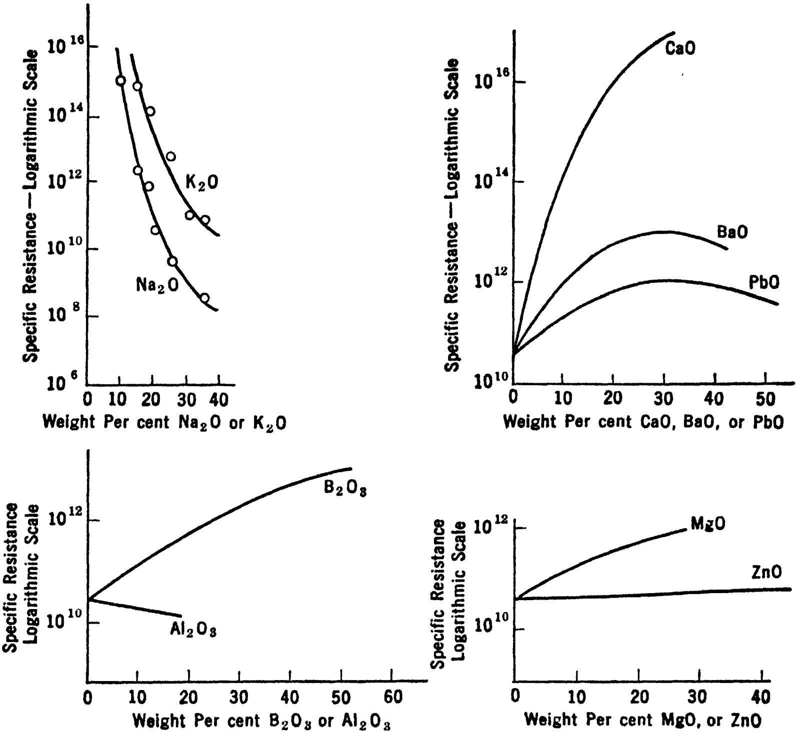

FIGURE XVII. 10.—The Effect on Specific Resistance of a Glass of the Composition $0.18Na_2O$, $0.82SiO_2$, of Replacing SiO_2 by the Indicated Percentage by Weight of Other Oxides. After Fulda.

The Effect of Temperature on Electrical Conductivity

The electrical conductivity of glass increases rapidly with temperature, the specific resistivity of some glasses decreasing from 10^{12} to 10^{15} or higher to around 10^{4} ohms at the annealing temperature, reaching unity at 1200° to 1500°. The variation of specific resistivity with temperature is well shown by the curve of Fig. XVII. 11 reproduced from

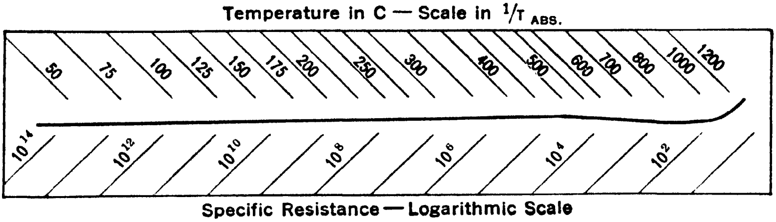

FIGURE XVII. 11.—The Change in Specific Resistance of a Glass with Temperature. After Fulda.

Fulda,[44] in which the logarithm of the specific resistivity is plotted against $1/T$, the reciprocal of the absolute temperature. From 25° to 460° the curve is a straight line, represented by the formula:

$$\log W = (A/T) + B$$

deduced by Rasch and Hinrichsen [45] on a questionable basis from Van't

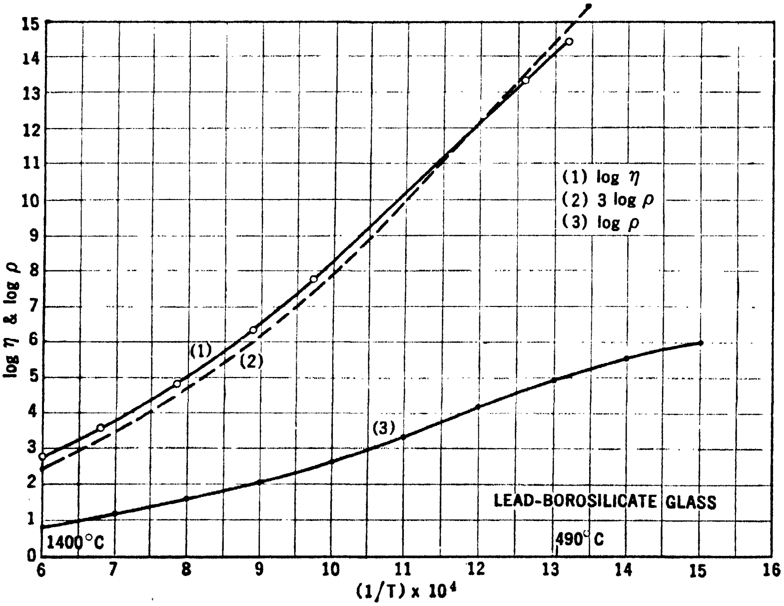

FIGURE XVII. 12.—Comparison of the Change with Temperature of the Resistivity and the Viscosity of a Lead-Borosilicate Glass. After Littleton.

[45] Rasch, E., and Hinrichsen, F. W., *Z. Electrochem.*, **14**, 41 (1908).

Hoff's equation. At 460° the plotted curve shows a break; from 460° to 650° the results are fitted by a second straight line; and above 650° the temperature coefficient decreases greatly. The Thuringian glass used had the composition: SiO_2, 71%; Na_2O, 12.5%; K_2O, 8.7%; CaO, 5.4%; Al_2O_3, 2.4%; and the constants A and B, respectively, for the middle range were 6.021 and 3.484. This is the only case in which the resistance of a glass has been determined from room temperature to 1200°.

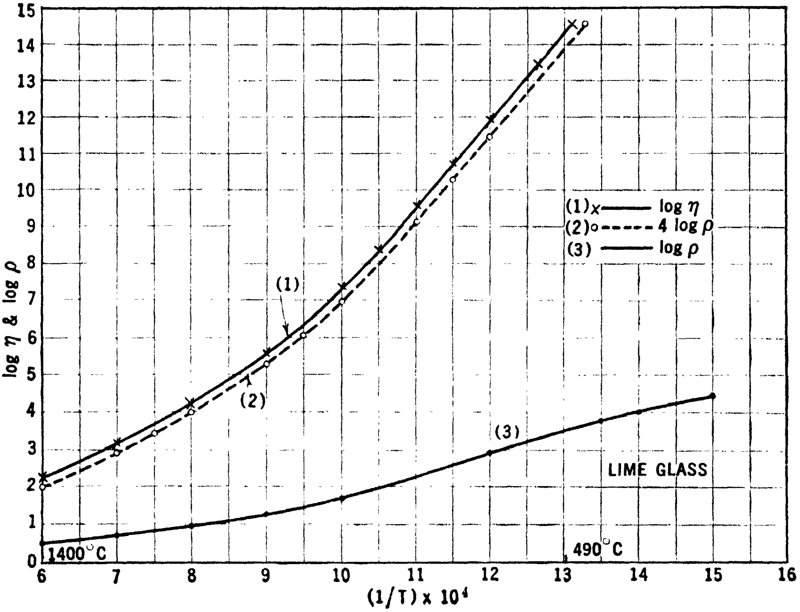

FIGURE XVII. 13.—Comparison of the Change with Temperature of the Resistivity and the Viscosity of a Lime Glass. After Littleton.

The break in the straight-line relationship between resistivity and the reciprocal of the absolute temperature, which is usually found near the temperature at which the glass is annealed, has been assumed to be of theoretical significance. The temperature so determined has been called the "transformation temperature" and has been proposed as a significant item in glass specifications. However, Littleton[46] has shown that this apparent discontinuity is due, not to a transformation, but to a delayed change in the properties of the glass. In the usual method, the glass is heated at the rate of 5° per minute. If the rate is diminished, the temperature of the break is altered; and if the glass is maintained at each

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[46] Littleton, J. T., *Ind. Eng. Chem.*, **25**, 748 (1933).

temperature until the conductivity has reached a constant value, the curve becomes a smooth one, without a break. Over a small temperature range the resistivity may be represented as a linear reciprocal function of the temperature; but over a large temperature range a real curvature becomes manifest. The viscosity apparently follows a similar law, although it changes much more rapidly with temperature than does the resistivity. Littleton compared the variation with temperature of viscosity and resistivity, and his results are reproduced in Figs. XVII. 12 to 15. With a lead borosilicate glass, shown in Fig. XVII. 12, the viscosity varies with the cube of the resistivity; with a lime glass, Fig. XVII. 13, it varies as the fourth power of the resistivity; with a lead glass, and with a borosilicate glass, Fig. XVII. 14, the relationship is of the form

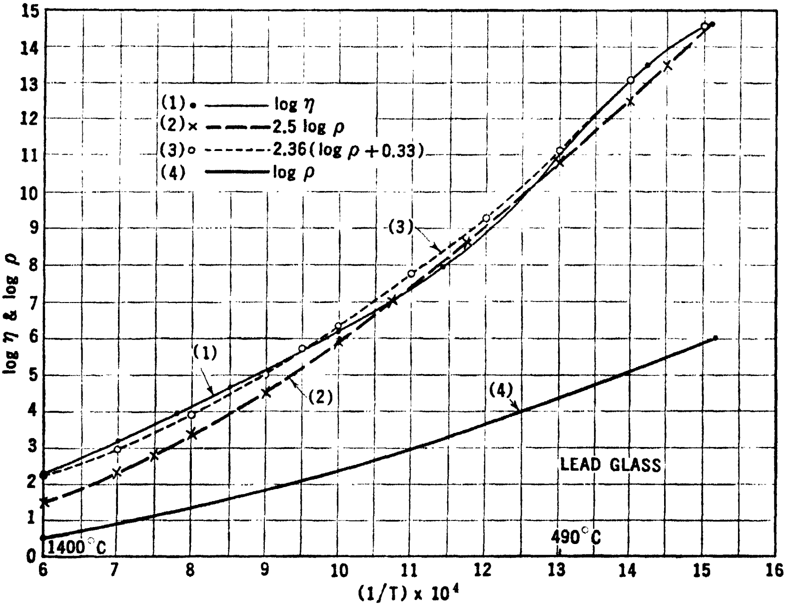

FIGURE XVII. 14.—Comparison of the Change with Temperature of the Resistivity and the Viscosity of a Lead Glass. After Littleton.

$$\log \eta = a \log w - b$$

or

$$w = b'\eta^{1/a}$$

Littleton and Wetmore[47] studied the change of electrical resistance with temperature, using a soda-potash-lead glass of high resistance used for lamp seals. The annealing point of the glass was 431° C., the strain

[47] Littleton, J. T., and Wetmore, W. L., *J. Am. Ceram. Soc.*, **19**, 243 (1936).

point,* 395° C. Direct-current voltage of the order of two volts per cm. was used, and polarization was avoided by using very low currents, of the order of 10^{-7} to 10^{-10} ampere, which were measured with a vacuum-tube potentiometer. The resistivity of "chilled" glass, "annealed" glass and "stabilized" glass was measured. The chilled glass was cooled in air from 450° C.; the annealed glass was cooled according to a temperature-time schedule which is given. The measurements leading to values of the "stabilized" resistance are shown in Fig. XVII. 16, and the value chosen at each temperature was the identical final value for the annealed and for the chilled sample, or the average of these two when they were not identical.

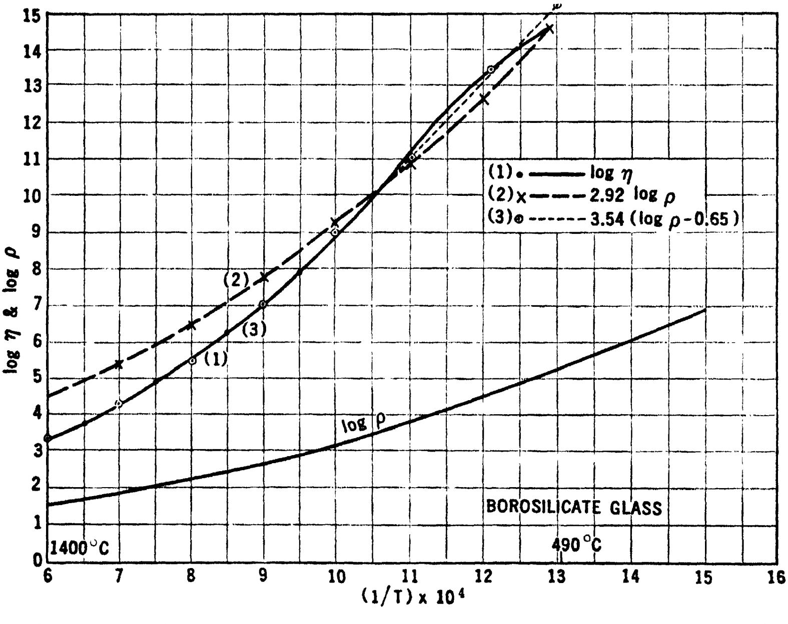

Figure XVII. 15.—Comparison of the Change with Temperature of the Resistivity and the Viscosity of a Borosilicate Glass. After Littleton.

All the chilled samples showed an increase in resistance with time, whereas the annealed samples at higher temperatures showed a decrease in resistance. This is due to the fact that the initial state of the chilled glass always corresponded to the equilibrium condition at a temperature higher than that of the experiment, whereas that of the annealed glass corresponded to a temperature below those of the experiments in which the resistance decreased.

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* Cf. p. 191.

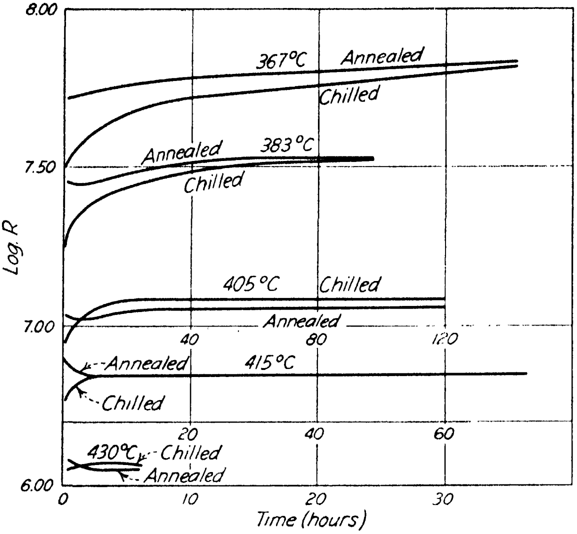

Figure XVII. 16.—The Change with Time of the Electrical Conductivity of Chilled and Annealed Glasses. After Littleton and Wetmore.

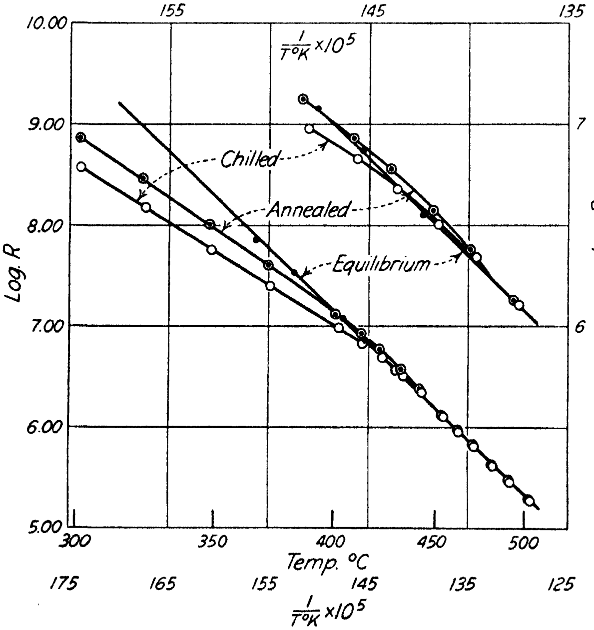

Figure XVII. 17.—Electrical Conductivity as a Function of Temperature of Chilled and Annealed Glass, and of Glass in the Equilibrium Condition. After Littleton and Wetmore.

The results obtained with the three types of heat treatment are shown in Fig. XVII. 17. The curve for the stabilized glass is a straight line to as low as the measurements extended, which was about 50° C. below the change-point temperature of the chilled glass. The part of the curves between the intersecting points is shown on an enlarged scale in the upper part of the diagram. The curves for the annealed and chilled glasses are not two straight lines intersecting at a point, as they are usually given, nor do the two curves gradually merge into each other. "The glass is stabilized at the temperature where the curves cross; the annealed and chilled glasses then lag behind in stabilization and finally catch up with the stabilized glass at the point where the curves coincide. This point of inflection has not been observed previously."

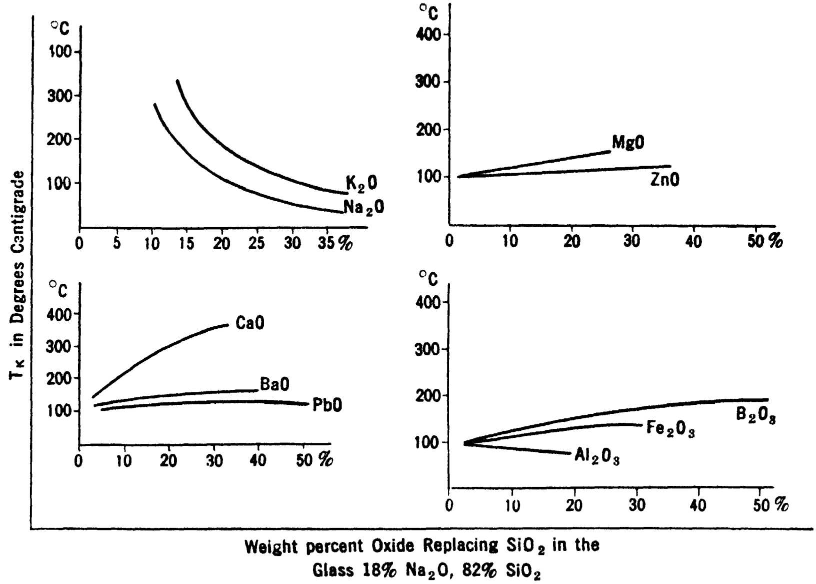

FIGURE XVII. 18.—The Change in Electrical Conductivity with Temperature of a Series of Glasses having the General Composition Na_2O (or K_2O), MeO, $6SiO_2$. After Gehlhoff and Thomas.

Gehlhoff and Thomas [48] made measurements in the temperature interval from 100° to 400° on glasses of systematically varied composition, some of which were studied further by Fulda.[44] Fig. XVII. 18 shows the variation in conductivity with temperature of a number of glasses of the general composition Na_2O (or K_2O) · MeO · $6SiO_2$, in which MeO

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[48] Gehlhoff, G., and Thomas, M., *Z. tech. Physik*, **6**, 544-54 (1925).

represents MgO, CaO, ZnO, BaO and PbO. The relation between temperature and resistivity followed the relation of Rasch and Hinrichsen.

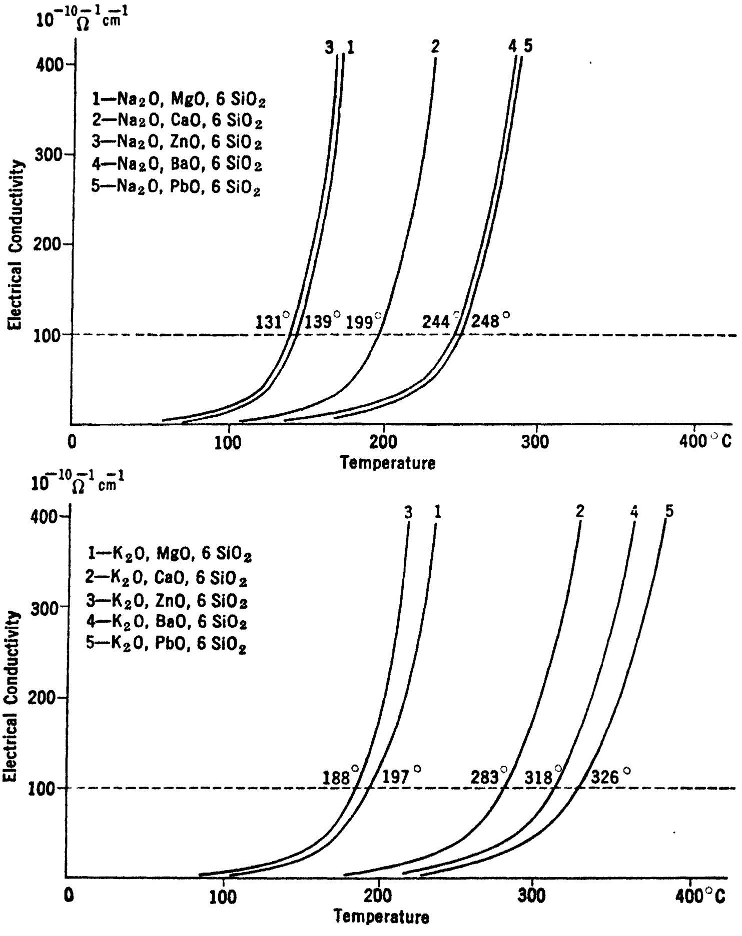

FIGURE XVII. 19.—The Temperature at which the Specific Conductivity Becomes 100×10^{-10} plotted against the Percentage by Weight of the Indicated Oxide Replacing SiO_2 in the Glass $0.18Na_2O$, $0.82SiO_2$. After Gehlhoff and Thomas.

In order to show the effect of variation in composition on the conducting power of glass, the temperature at which the specific conductivity, T_K, became 100×10^{-10} ohm^{-1} cm^{-1} was chosen for comparison. Fig. XVII. 19 refers to this arbitrary standard, and it shows that the alkalies greatly increase conductivity, Na_2O more so than K_2O. Al_2O_3 slightly increases the conductivity. ZnO, MgO, PbO, Fe_2O_3, BaO, B_2O_3 and

CaO decrease the conductivity, although all except CaO have but little effect. Studies of several series of four-component glasses containing both Na_2O and K_2O showed that the presence of both alkalies gave a poorer conducting glass than either alone, the minimum conductivity being at a $Na_2O : K_2O$ ratio of about 1 : 4. Gehlhoff and Thomas summarize their results in Table XVII.3 in which the average values of $T_K = 100$ for an addition of one per cent of the given oxide are given, for each five per cent composition range.

TABLE XVII. 3—The Change in $T_k = 100$, per 1% of Added Oxide, on Replacing SiO_2 by the Indicated Oxide, as Affected by Its Percentage in the Glass

After Gehlhoff and Thomas

Percentage Content of the Added Oxide

	0-5	5-10	10-15	15-20	20-25	25-30	30-35	35-40	40-50	50-60
B_2O_3	+ 3.0	+ 3.0	+ 2.8	+ 2.1	+1.3		+1.0		+0.9	
Na_2O ...			−27	− 9.4	−6.6	−5.4	−2.4			
K_2O			−36	−16.2	−8.6	−6.6	−5.6			
CaO	+14	+10	+ 8	+ 7.0	+6.6	+6.2				
BaO	+ 2.5	+ 2.3	+ 2.0	+ 1.7	+1.4	+1.0	+0.6	+0.3		
ZnO	+ 0.6	+ 0.5	+ 0.5	+ 0.5	+0.5	+0.5	+0.5			
PbO	+ 1.4	+ 1.3	+ 1.0	+ 0.7	+0.6	+0.4	+0.3	+0	−0.5	
MgO ...	+ 1.2	+ 1.4	+ 1.4	+ 2.3	+2.9					
Al_2O_3 ..	− 0.9	− 0.9	− 0.9							
Fe_2O_3 ...	+ 2.0	+ 2.0	+ 1.8	+ 1.3	+0.7					

Sutton and Silverman [49] measured the conductivity of a glass of the composition SiO_2, 67.37%; Na_2O, 15.60%; CaO, 16.74%; Al_2O_3, 0.41%; Fe_2O_3, 0.09%, from 750° to 1100°, as a part of their study of the effects of NaCl on the conductivity of glass. Their results are shown in Fig. XVII. 20.

Bryson [50] measured the conductivities of a number of experimental glasses from below 600° to 1150° using a frequency of 500 cycles. The composition of his glasses is given in Table XVII. 4, the conductivity results in Fig. XVII. 21. Detailed results were not given.

The work of Gehlhoff and Thomas, Fulda, and Bryson constitutes a beginning of the study of the electrical conductivity of glass as a function of the composition. As was emphasized in the discussion of density, it is not possible to deduce the effect of the various components of even a three-component system on the basis of a single short excursion into the ternary field, and so far there has been little even of that. The relationships become even more complicated with commercial glasses, which always contain several components concerning whose specific effect valid conclusions cannot be drawn. There is need of further study to ascertain the specific effects of the various components, the part

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[49] Sutton, W. J., and Silverman, A., *J. Am. Ceram. Soc.*, **7**, 86 (1924).

[50] Bryson, F. F. S., *J. Soc. Glass Tech.*, **11**, 331 (1927).

played by each in the process of conduction, and the effect of temperature on the conduction process.

Numerous other measurements have been made on the conductivity of glasses of various compositions and at various temperatures by Foussereau,[51] Thomson,[52] Bolle,[53] Ambronn,[54] Doelter,[55] and Baumeister.[56] Some of the measurements on known glass types are assembled in Table XVII. 5; the first group is by Bolle, the second by Baumeister. Bolle also measured three glasses whose compositions were near: SiO_2, 69%;

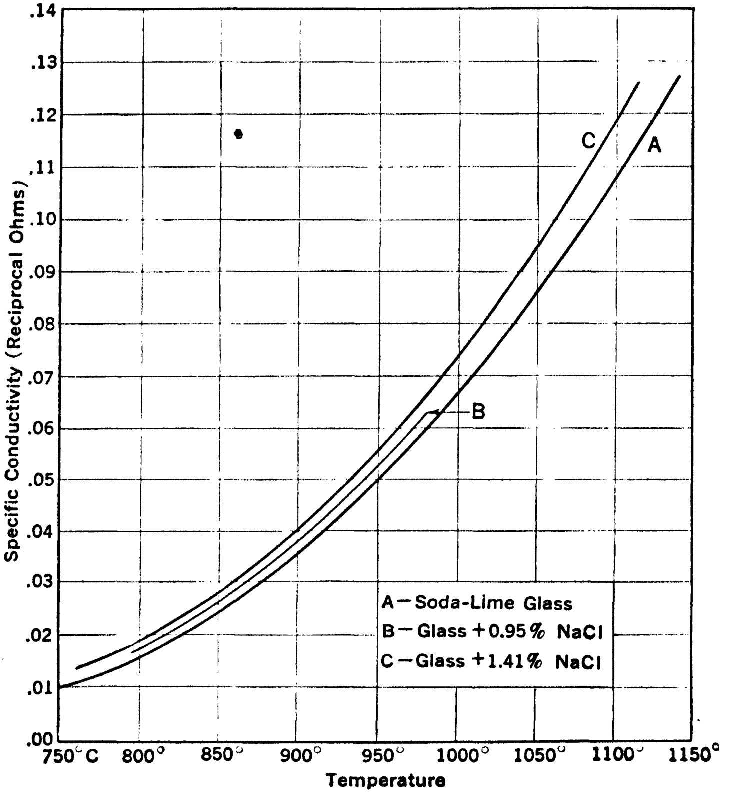

FIGURE XVII. 20.—The Change of Specific Conductivity with Temperature of a Soda-Lime Glass and the Effect of Addition of NaCl. After Sutton and Silverman.

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[51] Foussereau, G., *J. Phys.*, **11**, 254 (1883).

[52] Thomson, W., *Proc. Roy. Soc. (London)*, **23**, 468 (1875).

[53] Bolle, E., *Diss.*, Berlin (1900), cited by Eckert, F., *Jahrb. Radioakt. Elektronik*, **20**, 93, 190 (1923).

[54] Ambronn, R., *Physik. Z.*, **14**, 112 (1913); *Ann. Physik*, **58**, 139 (1919).

[55] Doelter, C., "Handbuch der Mineralchemie," **1**, 712, Steinkopff, Dresden u. Leipzig (1912).

[56] Baumeister, F., *Diss.*, Rostock (1912); *Fortschr. Physik*, **1**, 399 (1912).

Na_2O, 17%; ZnO, 5%; PbO, 8%; Al_2O_3, 1%, and found the following conductivities in ohms × 10^{10}: at 100°, 1.0; 150°, 17; 200°, 178.

Two of the obstacles to all physical measurements on glass are the difficulty of getting it into a reproducible state and the uncertainty as to what is to be taken as the standard state. The effect of annealing in all its aspects is an example, annealing not merely to remove mechanical strain, but also to define the state of the glass. This is a factor which has been insufficiently considered in the work which has appeared hitherto. It is known from the results of Foussereau,[57] of Fulda,[44] and of Mulligan, Ferguson, and Rebbeck[58] that annealing decreases the conductivity of glass; but no adequate study which separated the various factors involved has yet appeared. It is usually found that the ratio of resistivities of strained and annealed glass is at least 1:3. No adequate theoretical explanation has been advanced, and it is probable that none will be forthcoming until much more is known not only about the conduction process in glass, but also about the constitution of glass. Studies of the conduction process offer a promising method for the study of the constitution of glass.

TABLE XVII. 4—Compositions of Glasses Used by Bryson

Glass No.	SiO_2	Na_2O	CaO	MgO	Al_2O_3	Fe_2O_3
G 1 B	77.57	21.89			0.38	0.17
G 1 C	72.95	26.21			0.63	0.17
G 1 D	65.69	31.64		0.58	1.45	0.25
G 1 F	58.89	38.33		0.50	2.09	0.24
G 2 A	80.05	16.23		2.70	0.57	0.09
G 2 C	75.95	15.38	0.50	6.49	1.27	0.08
G 2 D	74.60	15.25		8.76	0.83	0.07
G 5 A	75.70	21.21		0.20	2.29	0.11
G 5 C	73.45	17.81		0.20	8.47	0.13
G 5 E	72.00	14.07			13.01	0.14

Another factor to be considered in precise measurements is the content of volatile components in the glass. Of these, water predominates, and that it, as well as the other volatile substances present, will exert a profound effect is highly probable. Bush and Connell[59] found that the volume resistivity was increased in a ratio of 6:1 by heating glass in vacuo to 350°; on exposure to air the resistivity again decreased. This opens an interesting field for future study and emphasizes the importance of precise definition of the composition of the glass studied, not only in regard to major constituents, but also in regard to accessory ingredients.

Sutton and Silverman[49] determined the effect of 0.95 per cent and 1.41 per cent NaCl on the conductivity of soda-lime glass, with the results shown in Figure XVII. 19. A satisfactory interpretation of such results is not possible with our present knowledge.

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[57] Foussereau, G., *Compt. rend.*, **96**, 785 (1883).

[58] Mulligan, M. J., Ferguson, J. B., and Rebbeck, J. W., *J. Phys. Chem.*, **32**, 779 (1928).

[59] Bush, V., and Connell, L. H., *J. Franklin Inst.*, **194**, 231-40 (1922).

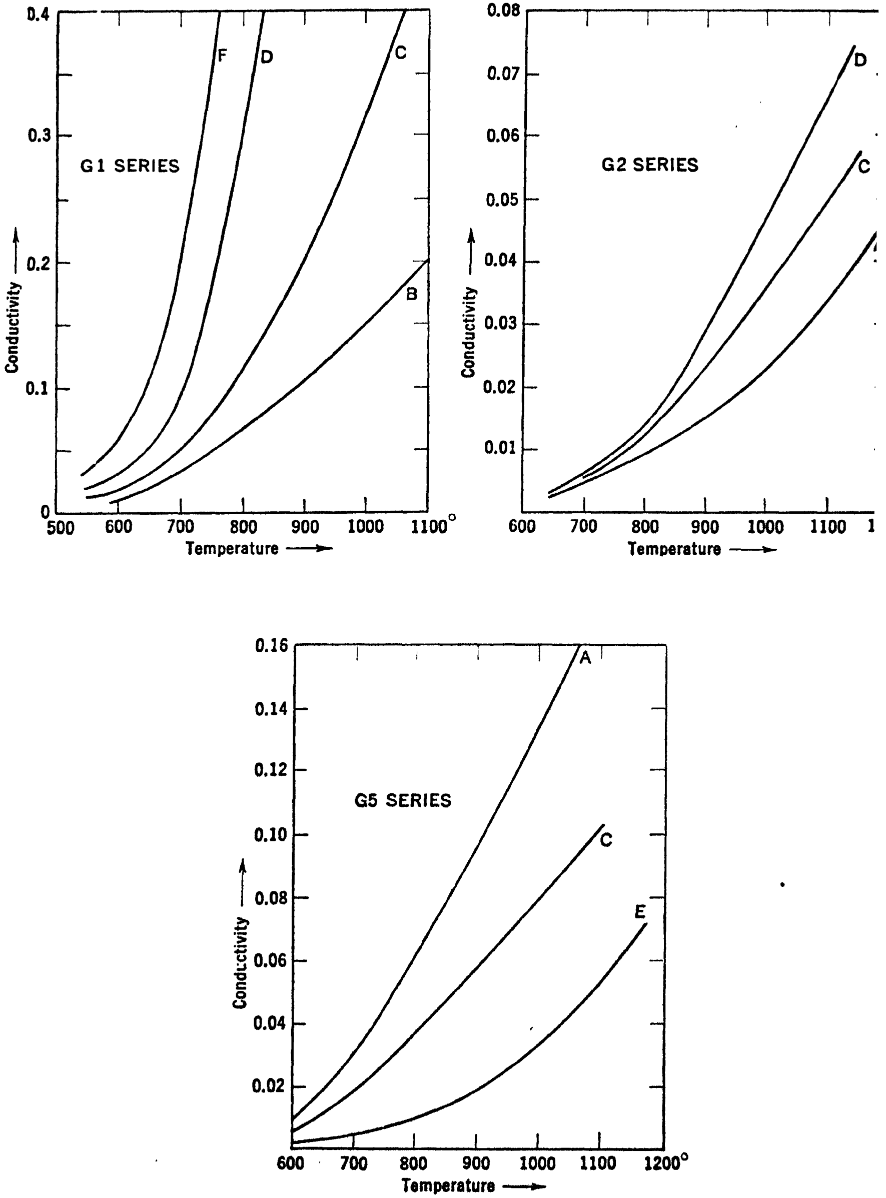

FIGURE XVII. 21.—The Change of Conductivity with Temperature of the Glasses of Composition given in Table XVII. 4. After Bryson.

Dielectric Absorption in Glass

Glass, in common with many dielectric materials, shows certain pecularities in its electrical behavior which are generally referred to under the title of "anomalous charging currents" or "dielectric absorption."[60] The designation of the effects as "anomalous" results from the observation that in this class of material the electric current which flows under a given impressed voltage is not a simple function of the temperature, the physical dimensions, and the conductivity of the sample, as is the case for the ordinary metallic or electrolyte conductors described by Ohm's law. Instead, in addition to the factors normally included in Ohm's law, the magnitude of the current flowing through the glass at any particular time is an undetermined function of the total elapsed time since the initial application of the voltage. So pronounced are these effects in glass that it is not surprising to find that it was probably the first material in which they were noticed, by Benjamin Franklin, who in 1748 described his observations on residual electrical charge in Leyden jars.

TABLE XVII. 5—Electrical Resistivity and Conductivity

(*a*) Resistivity

Pyrex Resistant Glass (No. 20, Table III. 3) Surface Resistivity;* 10^{14} ohms at 34% humidity; 5×10^8 ohms at 84% humidity. Volume resistivity,* 10^{14} ohm-cm.

(*b*) Conductivity, *K*

Comp. Ref., Table No.	Unit: 10^{12} ohm^{-1} cm^{-1} †				
	100°	125°	150°	175°	200°
III. 4. 4	0.012	0.0703	0.334	1.59	6.90
III. 4. 11	0.0132	0.0672	0.425	2.32	
III. 4. 18	0.00542	0.0418	0.221	1.57	7.69
III. 4. 21	0.0190	0.0416	0.0968	0.5076	2.38
III. 4. 60	0.0025	0.015	0.0684	0.668	2.544
III. 4. 27	0.00256	0.0134	0.0406	0.106	0.374
III. 4. 26	0.00233	0.00994	0.039	0.116	0.393

	Unit: 10^8 ohm^{-1} cm^{-1} ‡							
	t°	*K*	*t*°	*K*	*t*°	*K*	*t*°	*K*
III. 4. 56	250	12.9	402	400.8	502	1300	602	5000
III. 3. 4	250	0.677	400	41.58	489	210		
III. 4. 61	250	0.25	409	9.08	500	34.5	600	1178

* Corning Glass Works, Corning, N. Y.
† Bolle, Dissertation, Berlin (1900).
‡ Baumeister, Dissertation, Rostock (1912).

Because a dielectric such as glass at low temperatures cannot be made to act as a conductor of electricity without at the same time undergoing volume polarization, any system providing electrodes in contact with glass for the purpose of making conductivity experiments constitutes

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[60] For a summary and critical discussion of the theories of anomalous absorption currents in solids see lectures three to five inclusive (and extensive bibliography at end of book) in Whitehead, J. B., "Lectures on Dielectric Theory and Insulation," McGraw-Hill, New York, 1927.

a condenser, as do any two conducting electrodes separated by a dielectric. In the ideal condenser of classical theory, the application of a difference of potential to the plates produces a sudden surge of electric charge from one plate to the other. This charging process is over in a very short interval of time which can be accurately expressed in terms of certain constant physical properties of the ideal condenser by a definite mathematical equation. If this charged ideal condenser is suddenly short-circuited by connecting the plates, it discharges; its same physical properties once more serve to define the interval of time in which the process of discharge will be completed.

The behavior of an actual condenser in which the dielectric is glass, subjected to a similar charge and discharge cycle, may be contrasted to the ideal case as follows: Applying a difference of potential to the plates again produces a sudden surge of electric charge from one plate to the other. As this first surge due to the displacement current dies away, however, the flow of electric current into the glass condenser does not cease, as in the simple ideal condenser, but continues, the magnitude of this so-called anomalous charging current diminishing relatively slowly with time. This intermediate transient state of the charging current gives way in turn to a final steady state comparable to the conduction current in metals or electrolytes, though in general of a much lower order of magnitude. In this final stage the real condenser behaves as the ideal condenser might if a resistance, through which there would be a constant leakage current, were shunted across it. If the real condenser with glass dielectric be suddenly short-circuited, the discharge current, also, will differ in its behavior from the ideal condenser. The first impulsive rush of electricity is followed by a continued flow of current out of the glass, long after the displacement current of classical electromagnetic theory has died out. This so-called anomalous discharge current may be readily observed by removing the short-circuiting conductor and connecting the plates of the glass condenser to a sufficiently sensitive current-measuring device, which will indicate a reverse current coming out of the glass and following the same undetermined law of variation as the anomalous charging current. Furthermore, the anomalous charging current in glass is reversible, so that not only does the discharge current resemble the charging current in its manner of variation in time, but also its magnitude at any instant is that of the charging current, at the corresponding point in the charging cycle, diminished by the amount taken out by the final steady-state conduction current.

These same peculiarities in the electrical nature of glass may be examined in a different way by discharging a charged condenser, the dielectric of which is glass, and letting it stand for a short interval of time. Testing with a voltage detector then indicates that a potential difference has again established itself between the plates, and a so-called residual charge may be removed by again discharging the condenser. This process may be repeated several times before the absorbed charge is completely removed. This particular experiment was the one performed by Benjamin Franklin in 1748.

Since that time probably the most complete experimental investigation of dielectric absorption in glass was made by Hopkinson (1876-97). Among his numerous experiments on this subject, measurements of the above-mentioned residual charges in glass condensers, after a succession of charges and discharges at irregular time intervals and polarities, showed that anomalous charging currents and residual charges behave in accordance with the principle of superposition. Lord Kelvin was quoted by Hopkinson as saying, "the charges come out of the glass in the inverse order in which they go in." In Hopkinson's own words: "it seems safe to infer that the effects on a dielectric of past and present electric forces are superposable." This principle of superposition as exhibited in the behavior of anomalous charging currents in dielectrics such as glass may be stated as follows:

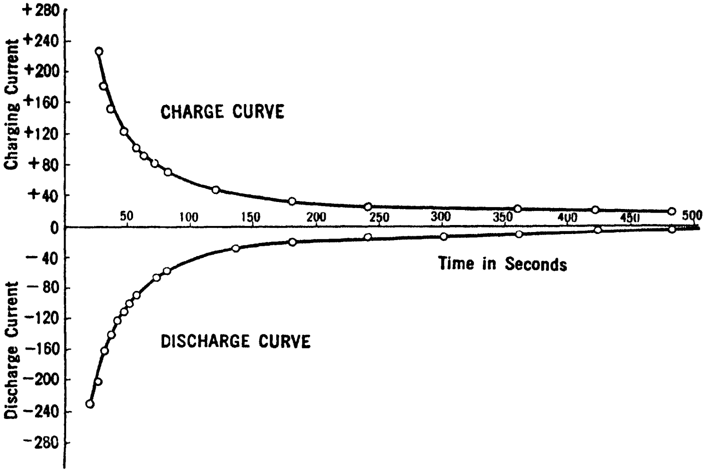

FIGURE XVII. 22.—Typical Charge and Discharge Curves of a Glass. After Guyer.

The variation in charging current resulting from several successive variations in the applied voltage is the summation of the individual variations in charging current which would have taken place if each voltage variation had been separately impressed upon the uncharged condenser.

That this important principle applies to the behavior of dielectrics such as glass, in which the absorption current is reversible, has been confirmed by numerous investigators since Hopkinson's time, in particular by J. Curie, who studied the electrical behavior of a variety of substances. Curie and Wilson both found that changes in applied voltage or thickness of the dielectric do not affect the time rate of variation of the absorption current but only its absolute magnitude, which is proportional to the voltage gradient, as is the true conduction current. Increases in temperature, on the other hand, increase both the magnitude and the time rate of variation of the absorption current. Guyer,[61] working at the Corning Glass Works Laboratory, has studied these various effects, and his results are given in Figs. XVII. 22, XVII. 23, XVII. 24. Fig. XVII. 22 shows typical charge and discharge curves for a borosilicate glass. The discharge curve of Fig. XVII. 22 shows only the ascending branch of the curve, but the discharge curve of Fig. XVII. 23, made on a somewhat harder glass, shows the initial descending branch, followed by reversal of the direction of current flow. Fig. XVII. 24 shows the effect of annealing on the charging current.

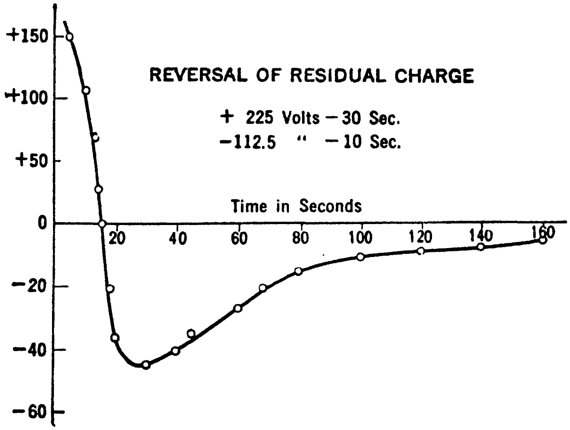

FIGURE XVII. 23.—Reversal of Residual Charge in a Borosilicate Glass. The charging cycle is given in the figure; readings were taken after disconnecting the charging battery. After Guyer.

An important implication of the principle of superposition as it applies to the electrical behavior, is that the true electrical resistance, in the sense implied by Ohm's law, of glasses in which there is a purely reversible absorption current may be determined as follows: (1) Measure the current through the glass when successive intervals of time have elapsed after the initial application of voltage to the sample. (2) Plot these data as a function of the time to obtain the characteristic

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[61] Guyer, E. M., *J. Am. Ceram. Soc.*, 16, 607 (1933).

charging curve of the glass under test. (3) Observe the discharge current at successive times, after the applied voltage has been removed. (4) Plot these discharge currents as a function of the time. (5) Compute for corresponding times the differences in the magnitudes of the observed currents in the charge and discharge curves, respectively. These differences will be constant for glasses in which the absorption current is purely reversible in character, and the current represented by this constant difference will be the true conduction current through the glass. Should the differences between the charging and the discharging currents, at equal time intervals, fail to remain a constant, this would mean that the absorption current was not purely reversible; and in consequence, the conduction current could be separated from the absorption current only by repeating the measurements at many successive intervals of time until the current had ceased to vary. In some instances the variations continue for hours.

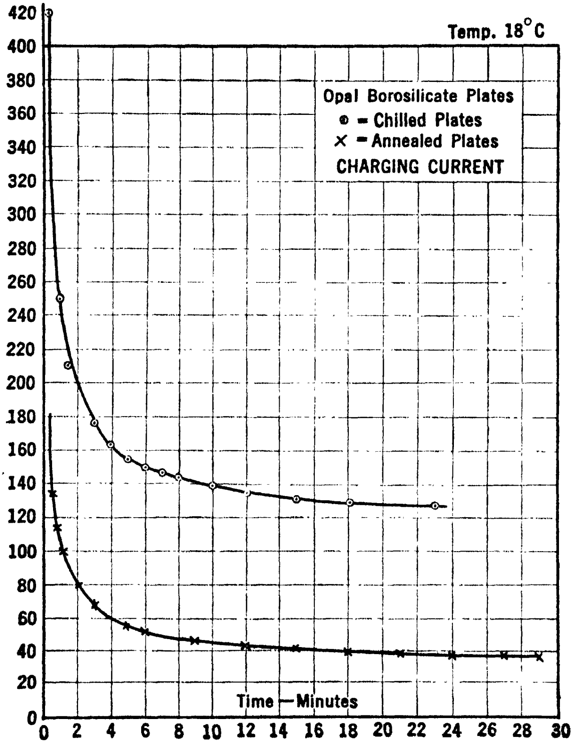

FIGURE XVII. 24.—Effect of Chilling and Subsequent Annealing on the Charging Current in an Opal Borosilicate Glass. After Guyer.

Any measurements of the electrical resistance of glass at low temperatures are likely to be seriously in error unless the absorption current is taken into account, because it may predominate over the conduction current. It is not sufficient to take measurements after a stated interval of time unless it has been previously shown that this time is sufficient to allow a complete decay of the absorption current.

In spite of the theoretical importance of this subject no complete study has been made of the absorption current in different glasses with the object of correlating this property with any known physical property or with composition. This may be due in part to the fact that there is no generally accepted adequate theory as to the nature of dielectric absorption.

Because more is known concerning the identity, the mobility and the ionic nature of the electrical carriers in glass than in most dielectrics, and also, since the absorption currents in many glasses have a time rate of variation which may be measured in minutes and hours, thus falling within a range of time which permits convenient and accurate measurement, this material offers opportunities for needed research along two lines: first, correlation of variations in dielectric absorption with changes in physical properties (electrical and mechanical) throughout a series of glasses of systematically varied composition; secondly, a study, in the individual members of this series, of the effects of systematically varied physical factors on the behavior of the absorption current. Not only might such a study yield data leading to a better understanding of the phenomenon of anomalous absorption in glass, but these same data would undoubtedly throw more light on the structure and ultimate nature of glass itself.

Chapter XVIII

The Dielectric Constant, Dielectric Loss, and Dielectric Strength of Glass*

Definitions and Units

It has been shown by experiment that the charge Q on a conductor is proportional to the difference in potential V between this conductor and the other conductors within the electric field of the charge; that is,

$$Q = CV \tag{1}$$

in which C is a constant called the capacitance. The whole system of conductors and insulating media is called a condenser. The capacitance is dependent both on the geometrical configuration and on the material of the dielectric; and if V_v is the capacitance of the condenser when the dielectric is a vacuum, and C is the capacitance with a different dielectric, then

$$C = C_v K \tag{2}$$

in which K is the dielectric constant of the substituting material. For air at low voltages $K = 1.0006$, or unity for practical purposes.

When an alternating current I flows into a condenser, charging it to a potential V, some energy is absorbed by the dielectric, resulting in the displacement current being not exactly 90° out of phase with the charging current; the difference in phase between current and potential is termed the "phase angle," θ. The "power loss" or "power factor," P, is given by

$$P = VI \cos \theta \tag{3}$$

or

$$P = VI \sin \delta \tag{4}$$

in which δ is the "phase difference angle" $(90 - \theta)$; for small angles $\sin \delta$ is approximately equal to δ.

Hoch[1] showed that the power loss per unit of volume is given by the relation

$$P/Ad = 2\pi fm \, (V/d)^2 K\delta$$

in which A is the area of the condenser, d is the distance between the

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* The discussion in the following pages is condensed from the monograph by Littleton, J. T., and Morey, G. W., "The Electrical Properties of Glass," Wiley, New York, 1933.

[1] Hoch, E., *Bell System Tech. J.*, **1**, 110 (1922).

plates, f is the frequency, and m is a constant depending on the units chosen. The measure of the dielectric loss in the material is not δ alone, but $K\delta$.

The dielectric strength of a material is the voltage required to puncture it, usually expressed in kilovolts per cm. or kilovolts per mil (0.001 in.). The dielectric strength is not a true material constant, hence the conditions of measurement, especially the thickness of the specimen, should be stated.

DIELECTRIC CONSTANT

The magnitude of the dielectric constant of insulating materials is of importance in the electrical industry. Usually, dielectrics of low dielectric constant are desirable for high-frequency insulation, and particularly for high-voltage insulation, in which application they diminish the stress on the air in series with the dielectric. A high dielectric constant is needed where maximum capacitance for a given size of condenser is desired, and under such conditions the total charge possible per unit of volume is a measure of the value of the material. With the possible exception of mica, which can be made in thin sheets, better condensers probably can be made from suitable glasses than from any other material. Glasses are unique among "solid" dielectrics because of their range of more than four to one in dielectric constant; and this wide range is of particular value when it is desired to match exactly the dielectric constant of some other material, as in condensers composed of glass and oil or wax. Moreover, glass is a valuable material for the development or testing of theories of dielectrics, because its compositions and properties to a limited extent are separately alterable.

Early Measurements of Dielectric Constant

Hopkinson[2] in 1878 made measurements on several glasses and found that the dielectric constant varied from 6.57 for a "very light flint" to 10.1 for "double extra dense" flint. He further observed for the same glasses, where K is the dielectric constant and s the density, that

$$K/s = 2.2 \text{ approximately.}$$

K was found to be constant up to gradients of 50 kv. per cm. and did not vary greatly with frequency. K increased by a factor of 2.6 as the temperature was raised from 25° to 170° C. with a frequency of 85 cycles; at 2×10^6 cycles the capacity was not affected by this temperature range; and at 8400 cycles the change was still very small. Hopkinson ascribed the effect at low frequencies to residual charge.

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[2] Hopkinson, J., *Trans. Roy. Soc. (London)*, 1878 (I), 17; 1881 (II), 355; *Proc. Roy. Soc. (London)*, 31, 148 and 347 (1881).

The work since Hopkinson's study has been mostly an extension of his experiments to many additional glasses. Much of this work is summarized in Tables XVII. 2 and XVIII. 4.

Dependence of Dielectric Constant on Frequency

The Maxwell equations for the electromagnetic waves lead to the relation $n^2 = K$, where n is the index of refraction of the medium and K, the dielectric constant, both measured for the same frequency. For this purpose it is necessary to know the dispersion of the medium; n measured for visible light is not to be compared with K measured for either d.c. voltage or low frequency, an error sometimes made.

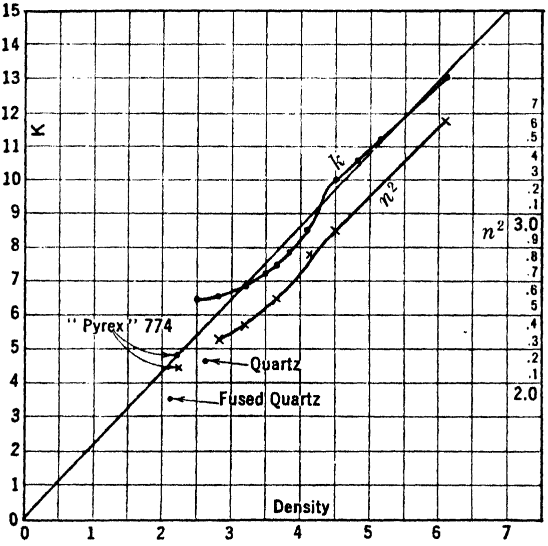

FIGURE XVIII. 1.—Variation of Dielectric Constant and Square of Refractive Index with Density. After Addenbroke.

The reflecting power R of a homogeneous isotropic material according to the Maxwell equations is given by

$$R = (n-1)^2/(n+1)^2,$$

and if $n^2 = K$ then K can be determined by measurements of R. This was done by Rubens,[3] who found that the values of R computed from measurements of K agreed very closely with the measured values. Rubens tested crystalline quartz, silica glass, ebonite, and a series of twelve glasses where K varied from 5.61 to 16.2.

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[3] Rubens, H., *Sitzber. kgl. preuss. Akad. Wiss.*, 1915, II, 1280.

Addenbrooke[4] compared the density with $(n_D)^2$ and K at a frequency of 150 cycles per second for seven glasses, and found that the ratio of K to n^2 varied from 2.75 to 3.55, with a range of K from 6.57 to 13.0. For the glass having a dielectric constant of 13 at 150 cycles, the value of $(n_D)^2$ was 3.68; since the change of apparent K is only from 13 to 3.68 for a frequency change of from 150 to 5×10^{14}, it is to be expected that the change in K in the radio-frequency band should be small. This conclusion is in harmony with other experimental work. Addenbrooke's results are shown in Fig. XVIII. 1 together with some measurements on Pyrex chemical resistant glass made in the physical laboratory of the Corning Glass Works.

TABLE XVIII. 1—Dielectric Constant of Silica Glass

After Jaeger

	Vitreous Silica			Frequency	Wave-length, (Meters)
Specimen No.	12	13	(Mean of (12 and 13)		
Thickness, mm	2.027	1.909			(1 to 2)
K by method I	3.66	3.69	3.68	250	$\times 10^6$
K by method II	3.61	3.71	3.66	10^5	3000
K by method III	3.58	3.59	3.59	10^6	300
K by method IV	3.57	3.56	3.57	10^7	30 to 40
K by method V	3.80	3.80	3.80	3×10^7	10
K by method VI	3.72		3.72	10^5	3000
Mean of two groups of methods*			3.72		

* The mean of methods V and VI is given double weight as compared with the mean of methods I to IV. The values differ a little from the values published by the author, as there seem to have been some errors of transcription in his summarized table.

The measurements on silica glass collected and discussed by Sosman[5] are in Table XVIII. 1.

The results obtained by Rubens[6] and Jaeger[7] on a series of glasses are given in Table XVIII. 2; their data indicate that K for most glasses decreases only a very small amount with increasing frequency.

Schott[8] found a slight decrease of K with increasing frequency in some glasses, the maximum observed change in K being a decrease of about one-half per cent as the frequency was changed from 1.9×10^5 to 10^6 cycles. MacLeod[9] reported a four and one-half per cent decrease in K as the frequency was varied from 500 to 10^6 cycles. His measurements were made on two lime glasses and on Pyrex chemical resistant glass.

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[4] Addenbrooke, G. L., *Phil. Mag.*, **45**, 516 (1923).

[5] Sosman, R. B., "The Properties of Silica," 516, Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1927.

[6] Rubens, H., *Sitzber. kgl. preuss. Akad. Wiss.*, **38**, 556-567 (1917).

[7] Jaeger, R., *Ann. Physik*, (4) **53**, 409 (1917).

[8] Schott, E., *Jahrb. drahtl. Tel.*, **18**, 82-122 (1921).

[9] MacLeod, H. J., *Phys. Rev.*, **21**, 53 (1923).

TABLE XVIII. 2—Dielectric Constants of Several Glasses

After Rubens and Jaeger

Glass	Type	Density	n_D	Dielectric Constants for 3000 m	10 m	57 mm	0.3 mm
Clear plate		2.54	1.5301	7.16	7.10		
Black		2.69	1.5504	7.41	7.31		
Violet		2.53	1.5341	6.85	6.89		
Fluoride crown, O 7185	464/656	2.27	1.4637	5.84	5.78	5.64	5.54
Phosphate crown, S 367	516/640	2.59	1.5164	6.41	6.40	6.28	6.17
Uviol crown, UV 3199	504/644	2.41	1.5035	5.66	5.56		
Crown with higher dispersion, O 381 III. 4. 13	526/513	2.70	1.5262	6.95	6.90		
Heavy barium, O 1209 (O 1993) III. 4. 34	611/572	3.55	1.6112	8.19	8.21		
Medium barium, O 1266 (O 1353) III. 4. 33	604/494	3.50	1.6042	7.68	7.73		
Medium flint, O 118 III. 4. 36	613/369	3.58	1.6129	7.52	7.42	7.33	7.37
Heavy flint, O 255	717/295	4.46	1.7145		9.98	9.55	9.41
Lead silicate, S 461		6.01	1.9170	16.3	16.1	15.6	15.6

Effect of Temperature on Dielectric Constant

This effect has been investigated only to a very limited extent over a small range of temperature.

Gray and Dobbie[10] measured *K* for a series of eight glasses at two different temperatures; the data are given in Table XVIII. 3.

A glass having the composition SiO_2, 33%; Al_2O_3, 6%; B_2O_3, 12%; BaO, 48% had a value of *K* equal to 8.5 which did not change with temperatures up to 140° C.

Strutt[11] measured the effect of temperature on *K* for five glasses at

TABLE XVIII. 3—Effect of Temperature on Dielectric Constant

After Gray and Dobbie

Glass Type	Temp. (° C)	*K*	Density
Soda-lime	11	6.26	2.487
	129	6.79	
Soda-lime-didymium	22	6.93	3.11
	147	7.18	
Soda-potash 26% PbO	10	7.06	2.99
	130	7.90	
Soda 39% PbO	19	7.376	3.36
	130	7.44	
Soda 40% PbO	20	8.013	3.408
	140	7.302	
Potash 40% PbO	18	6.766	3.34
	140	7.05	
10.6 Potash 41% PbO	18	7.22	3.41
	140	7.42	
13.7 Soda 45% PbO	8	5.42	3.552
	130	5.69	

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[10] Gray, A., and Dobbie, J., *Proc. Roy. Soc. (London)*, **63**, 38-44 (1898); **67**, 197 (1900).

[11] Strutt, M. J. O., *Arch. Elektrotech.*, **25**, 715 (1931).

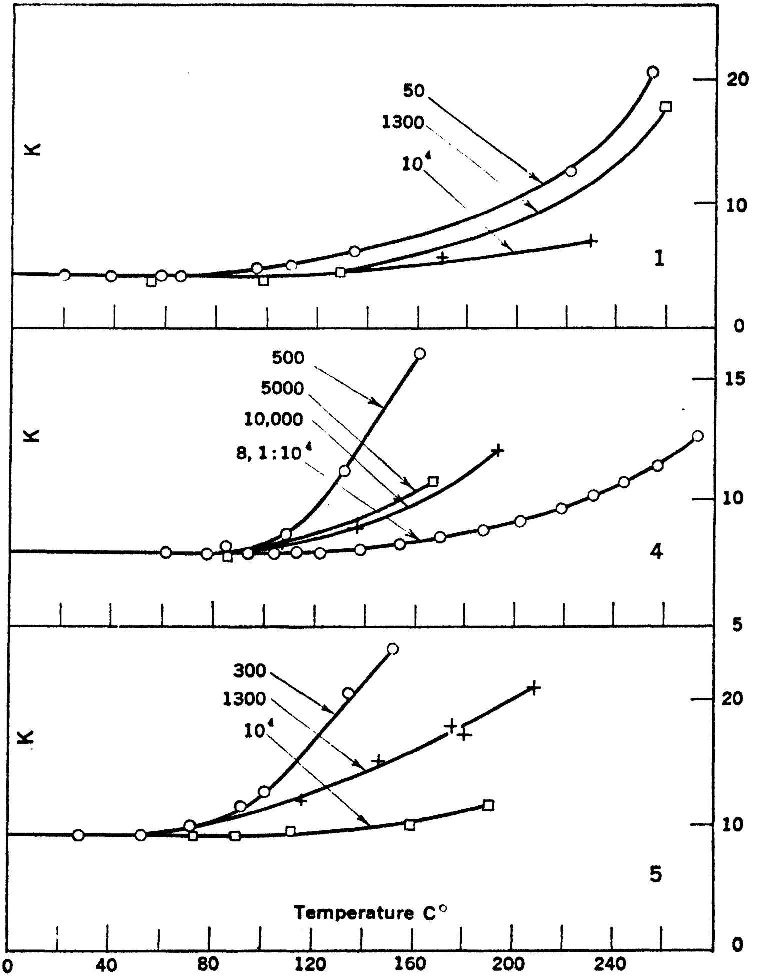

FIGURE XVIII. 2.—Dependence of Dielectric Constant, K, on Temperature at Various Frequencies. After Strutt.

different frequencies. Three of the curves obtained by Strutt are reproduced in Fig. XVIII. 2. Glass 1 is a borosilicate glass probably similar to Pyrex chemical resistant glass; 4 is a soda-lime glass of about 70 per cent SiO_2 and 16 per cent Na_2O; and glass 5 is "heavy lead glass."

These curves show that for each frequency the dielectric constant increases with increasing temperature, and in the case of low frequencies the displacement current rapidly becomes masked by the conduction current. Glass 1 should have a much higher electrical resistance than the other glasses, and this should be relatively less affected by temperature. The data show this to be the case. At higher frequencies *K* is not affected by temperature to the same extent as at lower ones.

The practical question as to the maximum operating temperature for a glass condenser accordingly depends upon both the composition of the glass and the frequency. For low frequencies about 80° C. approximates the limit of stability for lime glasses and 120° C. for the borosilicate type; for frequencies of the order of 10^4 cycles, lime glass is practically constant up to 140° C. and the borosilicate type to 240° C.

Leyden jar condensers have been frequently operated at high temperatures, but there seems to be no record of the temperatures used in such experiments. If, however, constant capacity is desired, the temperature should be kept below the limits cited above. Electrical failure caused by temperature rise is primarily a conductivity phenomenon, but the increase of *K* with temperature also is a contributing cause.

DIELECTRIC LOSS

The energy lost in a dielectric is measured by the angle δ between the current and the charging potential; it is often called the "Siemens" heat, in contrast to the usual Joule heat of d.c. practice. The amount of this loss is insignificant in power transmission lines, but with high-frequency currents it may be of importance. For condensers operated at high voltage and high frequency, low-loss materials should be selected. If a high capacity is desired, a material having a high dielectric constant furnishes this desired capacity with a smaller condenser volume, but the power loss per unit of volume is increased in proportion to the dielectric constant. If the voltage and frequency conditions are severe, then a material having both a low dielectric constant and a low power factor should be chosen, as this provides a lower energy absorption per unit volume and makes possible a greater area for energy dissipation.

Two general classes of glass are available, those having a high value of *K* and a low value of δ, and those having a low value of both *K* and δ; *K* and δ are separately alterable by change in composition. Table XVIII. 4 gives a summary of the measurements of *K* and δ for a number of glasses, with some information concerning composition.

Effect of Frequency on Dielectric Loss

Theory indicates that power factor should be a function of frequency, of the form [12]

$$P = B f^n$$

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[12] Schweidler, E. R. v., *Ann. Physik*, **24**, 711 (1907).

TABLE XVIII. 4—Power Loss in Glasses

After Several Observers

Lit. ref.	Glass	Frequency	K	δ	$K\delta \times 10^{-4}$
1	198b	6×10^5	11.3	0.00085	96
	102b	6×10^5	7.85	.00041	32
	103a	6×10^5	7.35	.000405	30
	118a	6×10^5	7.35	.000450	33
	318a	6×10^5	7.05	.000545	38
	340d	6×10^5	6.85	.00053	36
	3338a	6×10^5	6.26	.00113	71
	3439a	6×10^5	5.54	.00086	47
	3439b	6×10^5	5.37	.00098	53
	211a	6×10^5	7.41	.000755	56
	3453a	6×10^5	6.55	.0022	140
	3453a	6×10^5	6.64	.00231	150
	3832a	6×10^5	6.94	.002	130
	2188a	6×10^5	6.13	.0034	210
	15a	6×10^5	6.80	.00195	130
	3269b	6×10^5	8.46	.000432	37
	7550a	6×10^5	6.80	.00082	35
	381a	6×10^5	6.90	.00655	450
	5970c	6×10^5	8.07	.00065	52
	2994c	6×10^5	7.90	.000585	46
	1209d	6×10^5	7.80	.000555	43
	211k	6×10^5	7.50	.00078	59
	7185a	6×10^5	5.80	.00179	103
	S336a	6×10^5	7.05	.000505	36
	Quartz	6×10^5		.000117	
	Fused quartz	6×10^5	3.72	.000117	4.4
	O211	6×10^5		.000745	
	O211	4.3×10^5		.00072	
	O211	3×10^5		.00071	
	O211	1.87×10^5		.00695	
	O 15	6×10^5		.0019	
	O 15	4.3×10^5		.00183	
	O 15	3×10^5		.00175	
	O 15	1.87×10^5		.00173	
	T163	6×10^5		.00319	
	T163	43×10^5		.00308	
	T163	3×10^5		.00303	
	T163	1.87×10^5		.00298	
	S	55		.0195	
	S	6×10^5		.0051	
	S	4.3×10^5		.00517	
1	S	3×10^5		0.00525	
	S	1.87×10^5		.00540	
	O381	1×10^6		.00635	
	O381	6×10^5		.00664	
	O381	4.3×10^5		.00697	
	O381	3×10^5		.00710	
	O381	1.87×10^5		.00755	
	"Lead glass"	55		.0013	
	Do.	1,000		.00102	
	Do.	2,000		.000875	
	Do.	"high frequency"		.00082	
2	Pyrex chem. resist. glass	1,000	5	.0082	400
	Do.	1,000		.0113	(glass strained)
3	Do.	596		.0137	

TABLE XVIII. 4—(*Continued*)

Lit. ref.	Glass	Frequency	K	δ	$K\delta \times 10^{-4}$
3	Do.	1,010		.0127	
	Do.	2,920		.0111	
	Do.	14,000		.00889	
	Do.	100,000		.00743	
	Do.	500,000		.00666	
	Do.	750,000		.006778	
4	Do.	5×10^5	4.9	.0042	200
5	Do.	10^3	4.89	.0082	401
	Do.	3×10^4	4.83	.0056	270
6	Do.	20	4.88	.0065	316
	Do.	40	4.875	.0055	2.68
	Do.	80	4.80	.0052	254
7	Do.	7.15×10^5	5.8	.0052	
9	Do.	7.40×10^5	4.87	.0041	200
	Do.	10^6	5.0	.0038	190
	Do.	1.7×10^7	5.25	.0063	330
11	Do.	7.4×10^5	4.8	.0040	192
10	Do.	10^3		.00835	
	Do.	3×10^3		.00705	
	Do.	10^4		.00636	
	Do.	3×10^4		.00587	
	Do.	5×10^4		.00577	
	Do.	7.5×10^4		.00569	
	Do.	10^5		.00575	
3	No. 1	498		.00395	
	Do.	1,015		.00368	
3	No. 1	2,820		0.00327	
	Do.	14,000		.00276	
	Do.	10,000		.00236	
	Do.	500,000		.00213	
	Do.	100,000		.00198	
3	No. 2	498		.0169	
	Do.	1,015		.0149	
	Do.	3,130		.0124	
	Do.	1.4×10^4		.00974	
	Do.	10^5		.00766	
	Do.	5×10^5		.0066	
	Do.	10^6		.00617	
4	Flint	5×10^5	7	.0042	
	Do.	7.2×10^5	7	.0042	
	Do.	8.9×10^5	7	.00403	
	Plate	5×10^5	6.8	.007	475
	Cobalt	5×10^5	7.3	.007	510
5	1	10^3	8.7	.00735	6340
		3×10^4	7.9	.0298	2370
	2	10^3	8.2	.0280	2290
		3×10^4	7.9	.0122	960
	3	10^3	8.0	.0175	1400
		3×10^4	7.8	.0105	820
	4	10^3	8.2	.0245	2000
		3×10^4	7.9	.0175	1380
	5	10^3	8.1	.0228	1845
		3×10^4	7.8	.0122	955
	6	10^3	8.0	.0157	1260
		3×10^4	7.8	.0122	955
	7	10^3	6.8	.0047	319
		3×10^4	6.7	.0035	235
	8	10^3	7.2	.0157	1130

TABLE XVIII. 4—(*Continued*)

Lit. ref.	Glass	Frequency	K	δ	$K\delta \times 10^{-4}$
		3×10^4	7.0	.00885	1118
	9	10^3	5.2	.0065	338
		3×10^4	5.1	.00577	295
	11	10^3	4.7	.0049	230
		3×10^3	4.7	.00262	123
2	1	10^3	7.5	.0132	990
	3	10^3	6.8	.0031	210
	6	10^3	5.3	.0022	116
	4	10^3	4.7	.0039	183
2	5(Corning 707)	10^3	4.1	0.00077	31
11	Corning 707	7.4×10^5	4.4	.00069	30
9	Do.	7.4×10^5	4.16	.0006	25
	Do.	10^6	4.16	.0006	25
	Do.	1.7×10^8	4.12	.0017	70
7	Do.	7.15×10^5	4.4	.0005	22
8	Do.	3×10^4	3.88	.00060	23

1. Schott, E., *Jahrb. Z. drahtl. Tel.*, **18**, 82 (1921) (Jena Dissertation, 1921).
2. McDowell, L. S., and Begeman, H. L., *Phys. Rev.*, **31**, 476 (1928).
3. MacLeod, H. J., *Phys. Rev.*, **31**, 53 (1928).
4. Hoch, E., *Bell System Tech. J.*, **1** (Nov., 1922).
5. Decker, W., *Elec. World*, March 19, 1927.
6. Dawes, *Elec. World*, June 23, 1928.
7. U. S. Bur. Standards.
8. An industrial research laboratory.
9. R.C.A. Radiotron Co.
10. Yager, W. A., and Morgan, S. O., *J. Phys. Chem.*, **35**, 2026 (1931).
11. Corning Glass Works.

in which P is the power factor, f is the frequency, and B and n are constants. In general the measurements agree. MacLeod[9] studied three glasses and found the power factor to decrease by a factor of two to three as the frequency changed from 500 to 10^6 cycles. McDowell and Begeman[13] studied the change of power factor of six glasses, over a frequency range of from 800 to 4000 cycles, except for one glass, with which measurements were made to 1500 kilocycles. They found that, for frequencies from the audio range up to 100 to 200 kc., the von Schweidler equation was valid; but above 700 kc., the power factor of one glass (their No. 1, Table XVIII. 4) passed through a minimum (Fig. XVIII. 3).

Decker[14] measured a series of eleven glasses at frequencies of 10^3 and 3×10^4. All glasses showed a decided decrease in power factor as the frequency was increased.

Schott[15] made some measurements on three glasses which showed a power factor decreasing with increasing frequency. His "S" glass at "low frequency" (probably 55 cycles) was measured by Cohn and had $\delta = 0.0195$. The Schott measurements given in Table XVIII. 4 show that at 1.87×10^5 cycles, $\delta = 0.0054$ and decreased to 0.0051 at 6×10^5 cycles. The value of δ for the Schott glass O381 changed from 0.00755

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[13] McDowell, L. S., and Begeman, H. L., *Phys. Rev.*, **33**, 55 (1929).

[14] Decker, W. C., *Elec. World*, **89**, 601 (1927).

[15] Schott, E., *Jahrb. Z. drahtl. Tel.*, **18**, 82 (1921).

to 0.00635 as the frequency was changed from 1.87×10^5 to 6×10^5 cycles.

The data cited all show a decrease of power factor with increase in frequency except for the McDowell and Begeman glass No. 1, which shows a reversal at 7×10^5 cycles. However, there are other measurements on other glasses which show the opposite effect. The glasses 0211, 015, and T163, as measured by Schott (Table XVIII. 4), show that the power factor increases in the frequency range of 1.87×10^5 to 4.3×10^5 cycles.

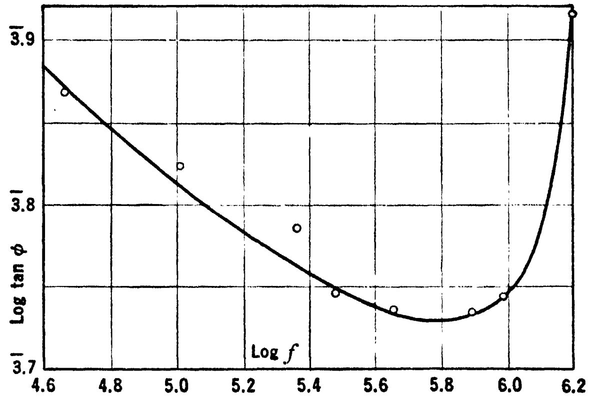

FIGURE XVIII. 3.—Relation between Power Loss and Frequency. After McDowell and Begeman.

Strutt[11] obtained very erratic results at room temperatures. At temperatures above 100° C. he found that the power factor always decreased as frequencies were varied from 50 cycles to 300 kc. His glass No. 1, which he called a "Pyrex type,"* gave the following values as taken from his curve at 20° C.

Frequency in cycles	50	160	500	1300	10,000
Power factor	0.0031	0.0018	0.002	0.0027	0.0048

These results indicate a very rapid change between frequencies of 50 and 160. No one else has observed any such abnormality in this zone. This is due possibly to some experimental error which is relatively larger with respect to actual power-factor values in the low-temperature low-loss zone, but which becomes relatively unimportant at higher temperatures where the dielectric losses are much greater.

In order to demonstrate the large discrepancies between the measurements of different observers, the different data on Pyrex chemical

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* This term means a glass having the characteristics of Pyrex chemical resistant glass.

resistant glass have been collected, and curves between the power factor and log frequency are shown in Fig. XVIII. 4. Where the data have been published, the author's name accompanies the curve. The other values are from unpublished laboratory reports. It is evident that the agreement is very poor. McDowell and Begeman[16] obtained values for

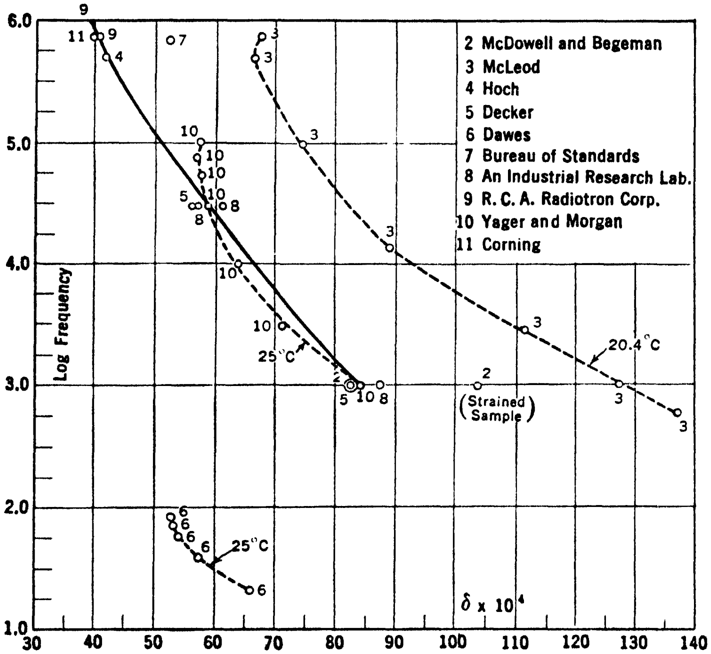

FIGURE XVIII. 4.—Relation between Power Factor and Frequency for Pyrex Chemical Resistant Glass.

strained glass almost twice that of annealed glass, so that possibly the state of annealing in the samples measured may account for a part of the difference between the results of the various observers. However, since the majority of the measurements have been made on stock samples that had had good commercial annealing, variations in annealing can account for only a very minor part of the discrepancies in the results. The discrepancies cannot be due to slight changes in chemical composition of the different samples. Unpublished measurements from the Corning Glass Works Laboratory show that a considerable variation in the composition of a given glass is required to cause changes in power factor of the magnitudes shown. Composition tests much more sensitive than power-factor measurements indicate no appreciable differ-

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[16] McDowell, L. S., and Begeman, H. L., *Phys. Rev.*, 31, 476 (1928).

ence between the various samples of the glass used in the power-factor tests. Comparison measurements also have been made on the glass by different laboratories over a period of years, and although the laboratories do not agree with one another, they always reproduce their own measurements within less than ten per cent. Also, some of the measurements reported by different laboratories were made on the same sample of glass.

The only conclusion to be drawn from these results is that in some glasses the power factor increases with frequency and in other glasses it decreases with frequency, with possible inversion points at frequencies above those of the measurements. It is possible that some of the measurements at the higher frequencies have been complicated by heating of the dielectric, which has resulted in an apparent increase in power factor.

The general conclusion is that experimental error in the measurement of low-loss glasses is very often quite appreciable, and that comparison of data from different laboratories cannot be made safely, even though the measurements are made on the same glass. In addition to the question of the accuracy of measurement, there is also that of the accurate knowledge of the chemical composition of the glasses measured. Unless this is known, a comparison of results by different observers is impossible. Probably differences in results between the different experimenters would have been more in evidence had the compositions of the glasses been published with the power-factor measurements.

Effect of Temperature on Power Factor

The variation of power factor with temperature is of interest for both practical and theoretical reasons. Power factor increases rapidly with rise in temperature, resulting in an increasing rate of energy absorption. As the temperature increases, the dielectric heating increases, and eventually the system becomes unstable, and breakdown occurs. This effect is of importance only in the case of high field strengths with the very high-frequency ranges, since only under such conditions is it possible for reasonably good dielectrics to reach the temperature of unstable equilibrium. In other cases, of course, it may be necessary to use the dielectric at elevated temperatures, and under such conditions it is essential to have some information as to the changes in the properties of the dielectric with temperature. The study of temperature effects is also of considerable theoretical significance. The application of such data to the development of dielectric theory has been of major interest to the workers in this field, and consequently the obtaining of what may be called engineering data has been neglected.

Schott,[15] McDowell and Begeman,[13] and Strutt[11] have discussed the relationship between electrical conductivity and power factor. The general conclusions are that at the lower temperatures power loss is due to a true dielectric loss with very little effect due to the ohmic resistance of the glasses, whereas at higher temperatures the resistance of the material decreases to such an extent that the conduction current is predominating.

Schott[15] found that the loss angle began to increase fairly rapidly after the temperature of 100° C. is reached, and that at 340° C. it had increased to about 40 times the value at 20° for a wave-length of 1600. Schott also made measurements down to − 80° C. and found a continual decrease of the power factor with decreasing temperature even in these lower temperature ranges. The resistance curve for this same glass showed how rapidly resistance changed with temperature, but there was no exact relationship between the power factor and the specific resistance. An increase in frequency or temperature caused a decrease in specific resistance whereas power factor increased with increasing frequency. The two properties therefore did not vary alike as temperature and frequency changed.

McDowell and Begeman[16, 13] studied the effect of change in frequency on power loss for six glasses at several constant temperatures, and the effect of change in temperature in the case of one glass over the range from 20° to 160° C., and also at − 186° C. Resistance measurements were made at temperatures from 20° to 500° C. and were found to follow accurately the equation $\rho = e^{k/T}$, where ρ is the specific resistance and T is the absolute temperature.

The comparison between power factor at 1000 cycles and specific resistance at 20° C. is given in Table XVIII. 5. Glass 6 had the highest resistance and glass 5 the lowest power factor. Except for glass 6, the power factor decreased as the resistance increased. The resistance was entirely too high to account for the power loss. The power factor at room temperature, computed from the conduction current, was negligibly small in comparison with the measured value.

TABLE XVIII. 5—Comparison between Power Factor and Specific Resistance

After McDowell and Begeman

Glass	ρ(20° C.)	Power Factor
1	2.3×10^{13}	0.0132
2	3.1×10^{14}	0.0082
3	2.0×10^{15}	0.0031
4	2.5×10^{15}	0.0039
5	3.5×10^{16}	0.00077
6	8.1×10^{19}	0.0022

The power factor increases with temperature owing both to the increase of the conduction current and to the increase of the absorption current. McDowell and Begeman[13] were able to correct their power-loss measurements for the portion due to conductivity. Their results on glass 2 are given in Fig. XVIII. 5.

Strutt[11] found a linear relationship between log tan δ and T as did McDowell and Begeman for their corrected values of tan δ. He further verified this relationship for the different frequencies, and his conclusions agreed with Schott's[15] in that the power factor increased with temperature more rapidly for low frequencies than it did for higher ones. The curves obtained by Strutt[11] are reproduced in Fig. XVIII. 6.

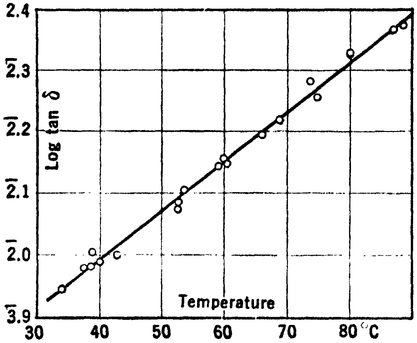

Figure XVIII. 5.—Relation between Power Factor, corrected for Conduction Loss, and Temperature. After McDowell and Begeman.

Hoch[1] gave data on Pyrex chemical resistant glass as follows:

Temperature (° C.)	K	δ	$K\delta$
20	4.9	0.0042	206×10^{-4}
74	5.0	0.007	350
125	5.0	0.0122	610
19	4.9	0.0044	216

These values were obtained at a frequency of 500 kc. It is evident that the power loss increased by a factor of approximately three for an increase of temperature of 100° C.

Relationship of Power Loss to Chemical Composition

The data on all glasses have been collected in Table XVIII. 4. As was stated above, comparison of the power-factor figures of different observers should be made with care. More reliance can be placed on the relative results obtained by any one experimenter.

It was concluded by Schott[15] that heavy metals such as lead and barium give low power factors and high dielectric constants, and that high alkali content gives high power factor. The compositions of the Schott glasses were not stated with sufficient exactness for com-

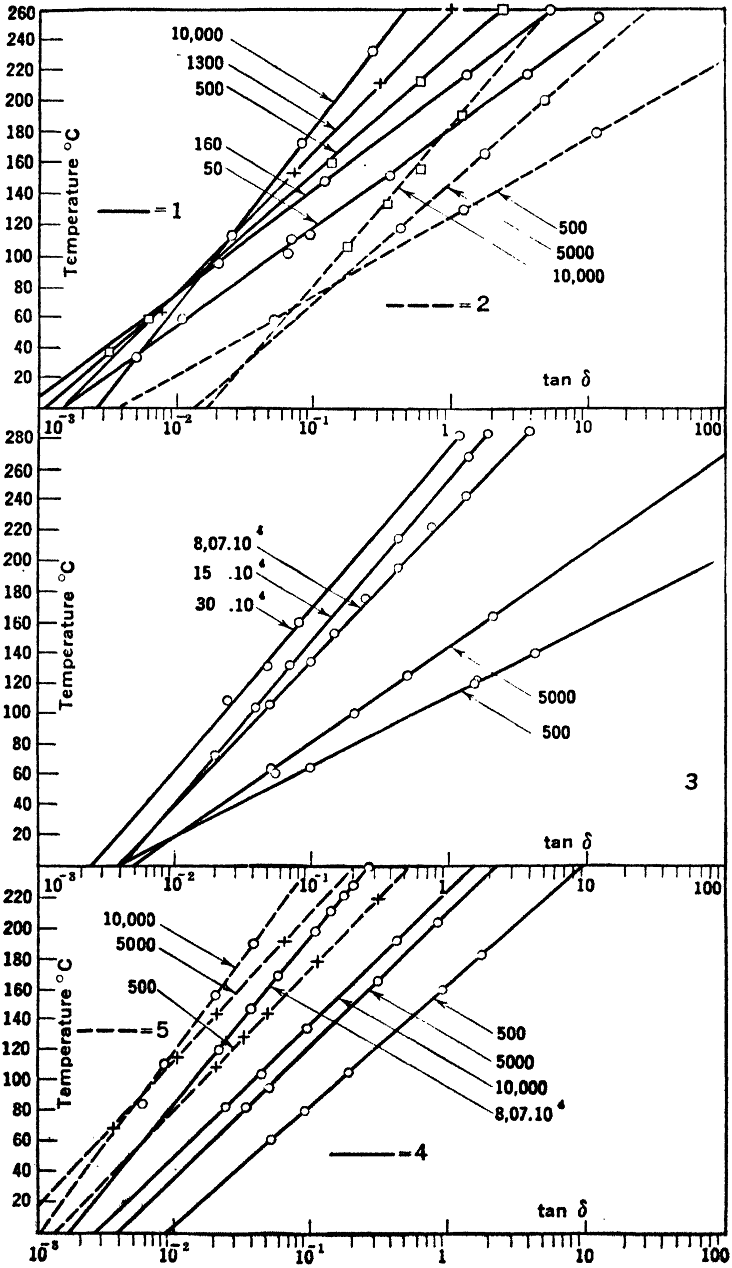

FIGURE XVIII. 6.—Relation between Temperature and Power Factor at Various Frequencies. After Strutt.

parison of his results with those of others or for independent conclusions as to the quantitative effect of the constituents of the glasses. To say that the alkali is "above" or "below" ten per cent is far from sufficient. Schott, so far as one can tell from his composition data, used only special glasses and made no measurements on any commercial insulator glasses. High-lead or high-barium glasses as a rule "weather" badly, that is, they are attacked by moisture; and they are relatively very expensive. He published no data on lime glasses. The glasses studied by Decker [14] were representative of commercial types, and complete analyses of the glasses were given. The enormous effect of alkali is made very apparent by Decker's measurements.

TABLE XVIII. 6—Dielectric Strength of a Glass in Various Oils

After Inge and Walther

Medium	Dielectric Constant	Specific Resistance	D. C. Breakdown Voltage, kv	50-Cycle Breakdown Voltage, kv_{eff}	Impulse Breakdown Voltage, kv
Pentane	1.8	7.5×10^{13}	12.8	6.65	7.7
Benzene	1.9	5.0×10^{12}	17.4	7.4	7.7
Transformer oil	2.2	7.4×10^{12}	16.9	7.4	7.9
Castor oil	4.4	2.3×10^{11}	18.4	7.4	7.4
Xylene	2.35	9.1×10^{10}	18.7	12.8	7.9
Xylene + 12% acetone	3.1	0.9×10^{8}	21.3	20.7	9.0

McDowell and Begeman also showed qualitatively the effect of alkali in increasing the power factor and the effect of lead in decreasing it. They concluded that power factor and electrical conductivity of glasses at elevated temperatures seem to vary alike, high-resistance glasses having the lowest power factors. This conclusion confirms that of Schott. However, the McDowell and Begeman glass 6 seems to be quite an exception to this generalization, as this glass had much the highest electrical resistivity, both at low and at elevated temperatures, and still had a power factor about three times that of their No. 5 glass. In general, however, power factor follows conductivity, and the conclusions regarding the effect of composition on conductivity may be expected to hold with respect to power factor.

High content of heavy metals in glasses with low alkali content gives high dielectric constant and low power factor. Borosilicate glasses with low alkali content, containing no heavy metals, have both low dielectric constant and low power factor, and hence low power-loss factor. Glass No. 5 in McDowell and Begeman's paper, which is Corning Glass Works glass 707, is the lowest-loss glass reported. The glass has this position because it combines low dielectric constant with low power factor. The low-alkali borosilicate glasses are in addition glasses of low expansion and of high surface stability. In other words, they combine in one material the necessary electrical property of good insulation, the other essential physical property of high thermal resistance, and chemical stability.

Dielectric Absorption, Dielectric Loss, and Power Factor

Mathematical theories have been advanced to explain, in terms of absorption and residual charge, the dependence of the properties of dielectrics on the frequency of the applied alternating voltage. Several of the most completely developed and widely accepted thories, although based on widely different pictures of the underlying mechanism, agree in postulating some form of exponential relaxation function relating the decay of the absorption current with time. In consequence, each of the several theories predicts values of the power factor which rise to a maximum and then decrease again with increasing frequency. This maximum has never been shown to exist in glasses, possibly because the power factor-frequency curve has never been obtained for any glass over a complete frequency range. Some measurements on some glasses indicate that power factor increases with frequency, whereas with other glasses the results indicate that power factor decreases with frequency. This apparent contradiction might be explained by assuming that the measurements are on opposite sides of the maximum point on the curve. For the ascending power factors they do not extend to sufficiently high frequencies to attain the maximum; for the descending values the frequencies are beyond the maximum power factor frequency. This conclusion, however, scarcely seems to be justified, since in the descending values the measurements have been made to as low as 40 cycles per second without a maximum being found; and in the ascending-power-factor glasses no maximum was indicated below 500 kc. It would be strange if in two similar glasses a maximum in one case lay below 40 cycles and in the other case above 500,000 cycles, and it is not improbable that the measurements indicating an ascending power factor are erroneous owing to an experimental error of the circuit, or to an increase of the power factor caused by dielectric heating of the glass.

From the nature of glass (that is, from its ionic conductivity, its homogeneous structure, its very great viscosity, and from the very slow rate of decay of its charging current, lasting in some cases for hours) one would conclude that the maximum point on the power-factor curve was at frequencies lower than have been studied. If the power factor of glass is determined largely by an absorption current following some form of exponential law of decay, as seems probable, then in the same frequency region in which a maximum value of power factor is to be expected, there should be also an apparent change in dielectric constant. Hopkinson found such a change in the "apparent capacity" of a glass condenser at room temperature in the range of very low frequencies. At a frequency of 7.3 cycles, the apparent capacity of a glass condenser was found to be approximately twice what it was at a frequency of 100. If this increase in capacity is an index of the general frequency region in which to expect a power-factor maximum, the absence in the literature of any observations indicating such a maximum would be accounted for by the maximum occurring in glass at room temperature at frequencies so small as to be far below the usual range of investigation.

Inasmuch as the physical constitution and properties of glasses can be varied by changes in composition and by heat treatment, it would appear that glass would serve as an ideal material for the study of the fundamental properties of dielectrics.

DIELECTRIC STRENGTH

If the dielectric strength of a material were a physical constant, it would be independent of the thickness of the material. Under the usual conditions of measurement it has been shown many times that, the greater the thickness of the test specimen, the lower is the measured dielectric strength of the material. The question as to what part of this effect depends upon the material and what part upon the method of test has not been answered, and much additional experimental information on this phase of the problem is required. Comparative tests of different insulating materials, even at the same thickness, probably lead to erroneous conclusions as to the relative strengths in service, and are valueless unless the tests exactly duplicate operating conditions. Such tests furnish no information as to the actual strengths of the materials, but only as to how the strengths are affected by the particular conditions of the experiment. The problem of measuring the strength of a dielectric in such a manner that the results can be applied to any set of operating conditions is an extremely fascinating one, but so far there is little fundamental information on "solid" dielectrics having breakdown strengths comparable to those of glasses. Although the data on glasses prove in general that very high potentials are required to produce failure under the test conditions, yet quantitative comparisons of different glasses and other materials should be avoided, unless the test conditions are identical.

Early Investigations

Almy[17] tested a series of five Jena glasses of known composition, and found the relation between thickness and puncture voltage to be given by the formula

$$V_{kv} = \alpha d + \beta$$

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[17] Almy, J. E., *Ann. Physik*, **1**, 508 (1900).

where V_{kv} is the breakdown voltage in kilovolts, d is the thickness in centimeters, and α and β are constants.

The puncture strength apparently was related in some way to the specific resistance, since, when the glasses were arranged in order of increasing dielectric strength, they were also in order of increasing specific resistance; but resistance changed manyfold, while the strength change was only a little more than twofold. Almy's tests were made under oil, and for that reason his data mean little. It later developed that it was necessary in dielectric-strength measurements to eliminate the electrode "edge effect."

The importance of the elimination of the edge effect was shown first by Moscicki [18] who proved that breakdown strengths of insulation as measured with electrodes immersed in oil to prevent flashover are valuless because the field strengths at the points of failure cannot be computed. The insulation always failed beyond the limits of the electrodes. This suggested to him the possibility of strengthening this zone sufficiently to produce failure under the electrodes. Since his experiments are so fundamentally important, it seems desirable to discuss his work in some detail.

Moscicki studied ebonite and three glasses; the glasses were (1) ordinary Bohemian alkali glass, (2) alkali-free glass from Schott u. Gen. No. 477^{III}, (3) borosilicate thermometer glass, Schott No. 59^{III}. His first experiments were made with 2-mm. glass plates under oil with tinfoil electrodes, and he found that all punctures took place beyond the edge of the foil at a voltage of 8 kv. He then experimented with a tube having a 0.3-mm. wall which served as one electrode, and having tinfoil on the outside as the other electrode. The tube was left sufficiently long so that the puncture test could be made in air without flashover. Under these conditions the puncture voltage was found to be 24 kv., a value three times that found for the plates used in the oil tests in spite of their much greater thickness. Other tubes with similar electrodes, when tested in oil, failed at 9 kv. at the edge of the coating. During the puncture tests in air he observed a corona ring at the edge of the tinfoil, and this he concluded acted as a semi-conducting region to diminish the field intensity and thus to increase the ultimate breakdown voltage. This observation suggested the possibility of protecting the end zones by increased insulation. Strips of mica were wound around these zones underneath the tinfoil edges, so that the mica thickness was gradually increased from the edge outward. The breakdown potential under oil thus was increased from 8 kv. to 17 kv., puncture still having taken place beyond the edge of the conductor through the mica.

In order to obtain a more gradual transition, a mixture of rosin,

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[18] Moscicki, J., *Elektrotech, Z.*, **25**, 527 (1904).

beeswax and Vaseline was built up under the edges of the tinfoil, great care being exercised to obtain the correct grading in thickness. Other tests were made with glass tubes having a thin blown section gradually increasing in thickness to the original wall of the tubes, with the addition, in some cases, of the insulating compound. The results with edge discharge present are shown in Fig. XVIII. 7; extrapolation to a thickness of 25 mm., or about an inch, gives a puncture voltage of 84 kv., much too low for the soda-lime glass used. A similar extrapolation of the results obtained with a borosilicate thermometer glass gives 100 kv. per inch, again much too low.

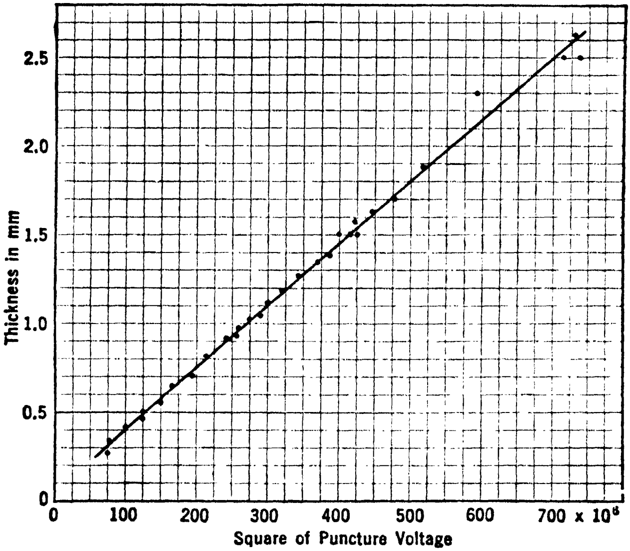

FIGURE XVIII. 7.—Relation between Thickness and Effective Puncture Voltage. Edge Discharge Present. After Moscicki.

When edge effect was present there was a linear relationship between the thickness of the glass and the square of the puncture voltage, as shown in Fig. XVIII. 7; but when the edge effects were suppressed the linear relationship was between thickness and the first power of the puncture voltage. The tests were made in air, and the punctures took place under the coating, which in this case was silver.

Moscicki[18] did not apply the voltage gradually, but used a 50-cycle transformer with a resistance in the primary. He adjusted the rheostat, then closed the circuit only long enough to get a voltage reading. In this way the voltage was increased to the point of failure by a series of increments. Undoubtedly there were many surges when the circuit was closed which his voltmeter did not indicate. The voltages given are the effective volts.

The dielectric strength obtained in this case was approximately six times that obtained on samples of the same thickness, when the electrode "edge effect" was not eliminated. These tests of Moscicki's[18] show how meaningless are the results of dielectric-strength tests on such insulator materials when the tests are made under oil. His experiments further prove that tests made under oil give no indication of the strength in air.

Additional tests made at 8000 to 9000 cycles without eliminating the edge effects gave values considerably below those obtained at 50 cycles, which were roughly two and a half times those at the higher frequency. Later work by others indicates that, when mercury electrodes are used, the adhering air film between the electrode and the dielectric should be removed under a vacuum. Probably Moscicki's results are somewhat low since he did not observe that precaution. In some cases he used silver-deposited electrodes, which it would seem should have given satisfactory results when failure occurred under the electrode. However, later work indicates that Moscicki's result of 1340 kv. per cm. is lower than the true strength. Hence it is concluded that even with silver electrodes the true strength is not necessarily attained.

The necessity for avoiding the electrode edge effect is very apparent. Other investigators, more recently, have avoided edge breakdown by various schemes. Rochow[19] used a biconcave lens of sufficient edge thickness to prevent puncture, and Inge and Walther[20] immersed their samples in xylene or in a mixture of xylene and acetone which eliminated marginal discharges. These measurements are discussed subsequently in more detail.

The Effect of the Surrounding Medium.

The measurements of Moscicki[18] show that the results of the tests are quite different when a preliminary failure of the surrounding dielectric occurs. Littleton and Shaver[21] made tests on commercial insulators under transformer oil, which showed that in dry high-strength oil the insulators failed under voltages about two-thirds of those they had previously withstood in air at 60 lb. per sq. in. pressure. Insulators tested in transformer oil containing a very slight amount of moisture (just enough to prevent marginal discharge at the voltages of the test) withstood without failure about twice the voltage required to puncture them when in the dry oil. Castor oil having nearly the same dielectric constant as the insulator was tried also, but the results were the same as with transformer oil; that is, the effect of the oil depended on the

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[19] Rochow, H., *Arch. Elektrotech.*, **14**, 361 (1925).

[20] Inge, L., and Walther, A., *Arch. Elektrotech.*, **19**, 257 (1928).

[21] Littleton, J. T., and Shaver, W. W., *Elec. World*, **91**, 759 (1928).

dielectric strength of the oil and not, so far as could be observed, on the relative dielectric constants of the two insulating media. Of course, it is possible that immediately surrounding the electrodes the dielectric constant of the medium at the voltages used might have been very greatly different from its low-voltage value.

Inge and Walther[20] made a comparison of the effect of oils of known properties. Their results on cover glasses 0.075 mm. thick are given in Table XVIII. 6. This glass probably had a dielectric constant of about seven.

The results with a.c. and d.c. voltages indicate that only the specific resistance of the medium is effective in eliminating preliminary breakdown of the surrounding medium. With impulse voltage the properties of the medium appeared to make no difference.

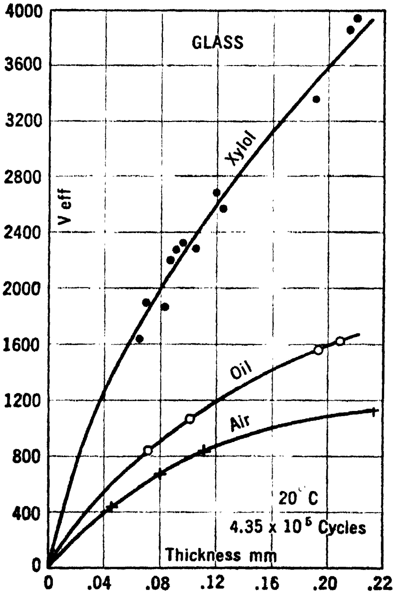

FIGURE XVIII. 8.—Relation between Thickness and Puncture Voltage, showing the Influence of the Surrounding Medium. After Inge and Walther.

In tests on plates at a frequency of 4.3×10^5 cycles, Inge and Walther[22] found that the medium had considerable effect (Fig. XVIII. 8). Tests on blown spheres, eliminating marginal discharge, gave approximately the same strength as was obtained for a 0.1-mm. plate in xylene.

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[22] Inge, L., and Walther, A., *Arch. Elektrotech.*, **21**, 209 (1928).

The effect of surface finish was also investigated. The results are as follows:

Polished	3000 kv. max. per cm.
Fine-ground	2360 kv. max. per cm.
Coarse-ground	480 kv. max. per cm.

When the specimens having the differently ground surface finishes were tested under oil instead of under xylene, the results were all the same. This indicated that the edge failure was not affected by the degree of surface polish.

The Effect of Frequency of Applied Voltage

The relative effects of direct current, low-frequency, high-frequency and impulse voltages are of both practical importance and theoretical interest.

For thin sections in uniform fields at room temperature, the puncture strengths under direct, 50-cycle alternating (peak voltage), and impulse potentials are the same when electrodes giving some cooling action are used for the test.

From the studies of Inge and Walther,[20] Moon and Norcross,[23] Kenny, Luery, and Moriaty,[24] and Jost [25] it is evident that high-frequency tests give considerably lower values of dielectric strength for glass than do low-frequency tests. This is ascribed generally to the internal heating due to the dielectric power absorption, and this fact of decreased dielectric strength is cited as significant evidence favoring the thermo-electric theory of breakdown. However, one can just as well postulate that a high-frequency voltage does more than heat the dielectric. The rapid periodic elastic displacement of the dielectric particles under high frequency creates more often a configuration favorable to the breakdown of the dielectric, which results in lower dielectric strength. Besides, the high-frequency alternations might well have some increased ionization effect apart from the increased thermal agitation.

In addition to the question of the effect of frequency and wave form for rapidly increasing voltages, there is the problem of the fatigue action due to continuously applied and intermittent loads. Contrasted with the fatigue effect there is the question of the effect of aging. These two should not be confused. Fatigue may be defined as the gradual weakening under stress with a return to normal when the stress is removed; aging is a permanent weakening of the material.

The effect of the duration of the load was studied by Inge and Walther.[26] The curves in Fig. XVIII. 9 show that a weakening under

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[23] Moon, P. H., and Norcross, A. S., *J. Franklin Inst.*, **208**, 705 (1929).

[24] Kenny, N. D., Luery, A. M., and Moriaty, J. D., *Trans. Am. Inst. Elec. Engrs.*, **51**, 404 (1932).

[25] Jost, R., *Arch. Elektrotech.*, **23**, 305 (1929).

[26] Inge, L., and Walther, A., *Arch. Elektrotech.*, **22**, 410 (1929).

load appeared after three seconds. After 1000 seconds the strength was about 50 per cent of the initial strength and appeared to have attained a constant value. However, the degree of weakening must be determined largely by the balance between the ratio of the development and the dissipation of heat, if this decrease in strength is a thermal effect. In other words, the amount of fatigue may depend on the particular conditions of the experiment rather than be a property characteristic of the material.

In no instance was there any evidence of an effect traceable to an aging of the glass. The evidence, though indirect, leads to the conclusion that no such effect exists. In the case of direct currents at elevated temperatures, such an effect is to be expected, owing entirely to electrolysis and the attendant change in the composition of the glass. Data bearing on this question were obtained by Jost,[25] who tested glass under successive impulses; and his conclusion was that if the specimen would stand as many as twenty impulses, it would stand an indefinite number. Jost, however, made all his tests under some insulating medium where electrode edge effects were present, and for that reason his results are difficult to interpret.

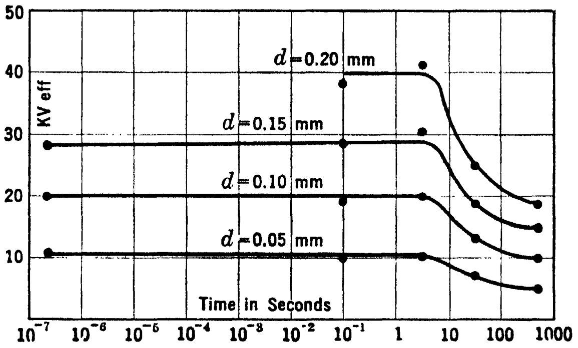

FIGURE XVIII. 9.—Effect of Duration of Load on Electrical Breakdown in a Uniform Field. After Inge and Walther.

The Variation of Dielectric Strength with Temperature

The effect of temperature on the dielectric strength of glass is of considerable importance from both the practical and the theoretical points of view. The Wagner[27] theory of dielectric failure is based on the fact that dielectrics such as glass become more conducting as their temperature increases. Wagner presupposes current flow and ohmic heating of the dielectrics, which become locally concentrated in a narrow zone or canal of initially slightly higher conductivity than that of the

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[27] Wagner, K. W., *Am. Inst. Elec. Engrs.*, 41, 288 (1922).

surrounding material. This conduction current heats the dielectric along this canal, which results in a decrease in resistance and in turn in a further increase in current. If the voltage is sufficiently high, this process leads ultimately to failure. Rogowski[28] determined the voltage-current characteristics of dielectrics, assuming uniform conductivity of the material and not the canal structure of Wagner. He found the heating theory insufficient to account for the facts observed during impulse failure and the failure of thin dielectrics; but at the same time, no purely electrical theory of failure was sufficient to explain the behavior of thicker materials under a continuous electrical stress. Accordingly he developed a thermoelectric theory from consideration of both the thermal effect and the purely electrical effect.

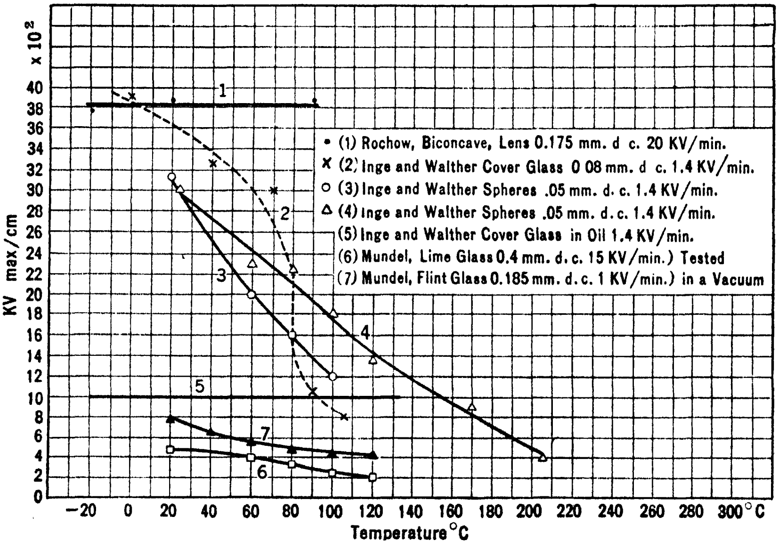

FIGURE XVIII 10.—Variation of Puncture Strength with Temperature.

Rogowski's theory assumes a maximum field strength in the material which cannot be exceeded without failure, and yet a dielectric in which heating caused by the conduction current is taking place. For short time intervals, and in thin plates having the surfaces cooled, the internal heating is small and failure will be due largely to the purely electric effect; but where the thickness is large and the heating appreciable, then thermal effects operate to produce the breakdown. These two theories of thermal action and the purely electrical theory have furnished

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[28] Rogowski, W., *Arch. Elektrotech.*, 13, 153 (1924).

the basis for the greater part of the studies of the effect of temperature on the dielectric strength of glasses.

Rochow,[19] using 50-cycle alternating current, found a constant strength for temperatures between − 18° and + 90° C. He eliminated edge effects by the use of glass samples in the form of biconcave lenses tested under xylene. He removed by evacuation all adhering gas bubbles from the mercury electrodes. He found that puncture occurred usually at the center of the electrodes, showing that edge effects were eliminated by this treatment. The glass tested was Jena flint glass O118 (No. 36, Table III. 4). His results for dielectric strength are given by curve 1, Fig. XVIII. 10. These results should be compared with those of Mündel,[29] whose measurements were made in a vacuum to prevent edge discharge. The data by Mündel on 0.4-mm. plates of a glass having the composition SiO_2, 70.6%; Na_2O, 16.8%; K_2O, 1.1%; MgO, 3.5%; CaO, 5.5%; BaO, 2%; R_2O_3, 0.5% are given in curve 6, Fig. XVIII. 11. This is a soda-lime glass with a high temperature coefficient of electrical resistivity, due to its high alkali content. Curve 7 by Mündel shows data on a "flint" glass which is probably quite similar to the glass used by Rochow. It is apparent that this glass gave somewhat higher strengths than that in curve 6, but was still far from being equal in strength to the glass of Rochow. This cannot have been caused by the slower voltage application rate of Mündel (the rate of Mündel was 1 kv. per min. as compared to 20 kv. per min. for Rochow), since Mündel's own tests showed that a change in rate of voltage application from 15 kv. per min. to 0.04 kv. per min. varied the strength at 20° C. only from 430 kv. per cm. to 395 kv. per cm. At 110° C. the ratio of the dielectric strength values obtained at the two extreme rates of voltage increase was about 2 : 1. This leads to the conclusion that in the apparatus used by Mündel the heat loss from the insulator test-piece was very small, as it was largely surrounded by a metallic reflecting electrode which reduced radiation loss, and a vacuum eliminated conduction and convection losses. This conclusion is confirmed by the experiments of Inge and Walther,[22] who obtained a strength in vacuum of only one-seventh of that obtained when the specimen was tested under xylene. These particular tests were made with high-frequency currents, which might tend to accentuate the difference on account of the greater amount of internal heating.

Under the conditions of his tests, Rochow had almost no dielectric heating, as was proved by an optical test for homogeneity, sensitive enough to detect in the specimen a localized rise in temperature of 10° C. The specific resistance of Rochow's glass changed by a factor of 4 × 10^5 in the temperature range of the experiments, yet there was

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[29] Mündel, E., *Arch. Elektrotech.*, 15, 320 (1925).

no change in dielectric strength. According to the theory of Rogowski, puncture voltage should have changed by a factor of 630.

The mercury electrodes of Rochow controlled the increase in temperature of the glass. The measurements of Mündel accordingly do not represent the strength of the glass at the temperature stated, but only that of the glass at the unknown temperature just preceding puncture. Curves 2, 3, and 4, Fig. XVIII. 10, are taken from Inge and Walther,[20] curve 2 showing the results on cover glasses immersed in xylene as the insulating liquid, and curves 3 and 4 the results on thin hollow spheres having mercury electrodes. In all cases the surfaces of the test-pieces were maintained reasonably near the temperatures measured.

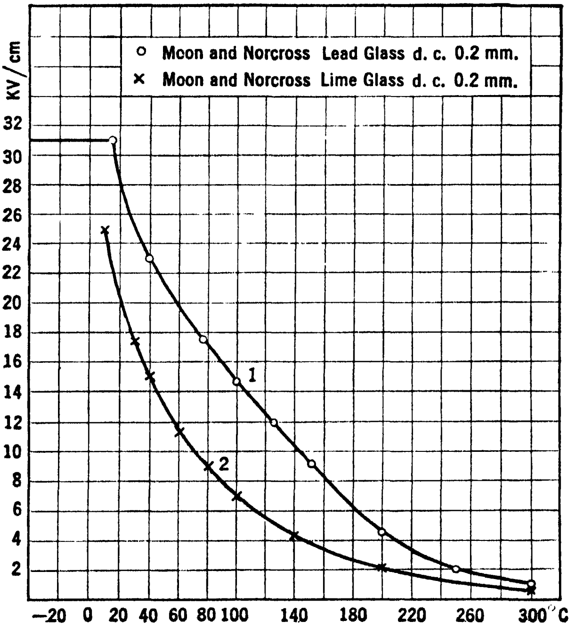

FIGURE XVIII. 11.—Change of Dielectric Strength with Temperature. After Moon and Norcross.

Curves 1 and 2, Fig. XVIII. 11, show data obtained by Moon and Norcross [23] on a lime glass and a lead glass. Curve 2 was obtained with plates immersed in insulating liquids and curve 1 with thin spheres. In both cases, rise of temperature of the glass was retarded by the cooling of the medium and of the electrodes. The authors stated that the rate of voltage increase was uniform and adjusted so that the time of application preceding puncture was about ten minutes. Their preliminary tests proved this factor to have no effect on the puncture voltage.

The relation between log V and $1/T$ is shown by the dotted curves in Fig. XVIII. 12 with the original curves of Moon and Norcross reproduced for comparison; the demarcation between the assumed separate regions, namely, a disruptive, an intermediate and a thermal region, evidently is arbitrary. This conclusion is in agreement with that of Inge and Walther. Kenny, Luery, and Moriaty,[30] following the same experimental procedure as Moon and Norcross except for using 60 cycles instead of direct current, stated that the observations were not sufficiently accurate to determine whether the transitions should be denoted by sharp discontinuities or by gradual transitions.

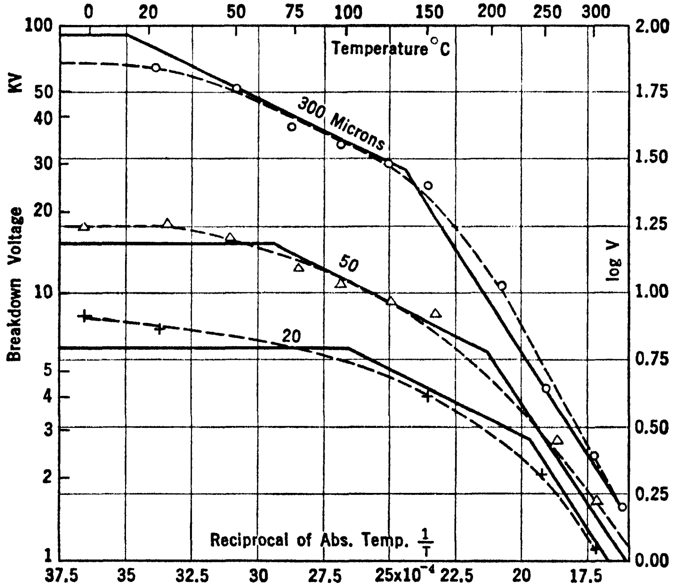

FIGURE XVIII. 12.—Relation between Puncture Strength and Temperature. After Moon and Norcross.

There seems to be some relationship between the specific resistance of a glass at high temperatures and its breakdown voltage. Inge and Walther[31] found that the glass with the higher resistance had the higher dielectric strength. The tests below 200° C. were made under oil.

The general conclusion from these measurements on thin glass plates is that the Rogowski thermoelectric theory serves as an interpretation of the observed facts, but that it cannot be quantitatively

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[30] Kenny, N. D., Luery, A. M., and Moriaty, J. D., *Trans. Am. Inst. Elec. Engrs.*, **51**, 404 (1932).
[31] Inge, L., and Walther, A., *Z. Physik*, **37**, 292 (1926).

verified, owing to lack of information as to the temperature of the specimens and the exact current and field distribution in the specimen under test. Any factor that increases the temperature of the dielectric, such as long-continued application of voltage, thermal insulation, or the application of high frequencies producing heating by dielectric loss, should decrease the puncture strength by an amount depending upon the change in temperature. The data cited seem to indicate that this is true.

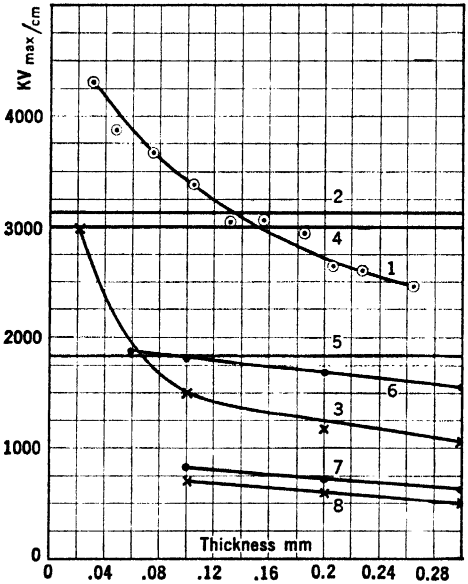

FIGURE XVIII. 13.—Variation of Dielectric Strength with Thickness.

(1) Data by Rochow. Flint Glass.
(2) Data by Moon and Norcross. Lead Glass, 20° C.
(3) Data by Moon and Norcross. Lime Glass, 20° C.
(4) Data by Inge and Walther. Cover Glass and Russian Apparatus Glass.
(5) Data by Moscicki.
(6) Data by Güllner.
(7) Data by Mündel. Flint Glass.
(8) Data by Mündel. Lime Glass.

Variation of Dielectric Strength with Thickness

In general, dielectric strength is supposed to decrease with increasing thickness. On account of the very high dielectric strength of glass, only comparatively small thicknesses have been studied. The data of different observers have been collected in Fig. XVIII. 13. Electrode edge effect is presumed to have been eliminated in all these tests.

It is apparent that the different investigators obtained widely different strengths, with no agreement as to a constancy of strength with thickness even in the very thin specimens tested. Inge and Walther found the same strengths for impulse voltage, direct current voltage, and the peak voltage of 50-cycle alternating current.

Relation Between Dielectric Strength and Composition of Glass

The previous discussions have shown the futility of attempting to draw any conclusions concerning the effect of composition on the dielectric strength of glass. Moon and Norcross[32] concluded that the dielectric strength in the disruptive region is proportional to the silica content of the glass. They worked with four different glasses of widely different composition, all containing four or more components in various proportions; so that their results do not furnish any information as to the effect of the separate components. The dielectric strengths obtained by them in the disruptive region were inversely proportional to the probable dielectric constants of the glasses, which might be of some significance; but also they were inversely proportional to the specific gravities and the indices of refraction, which probably is of no significance.

In the temperature zones where thermal failure occurs it probably will be found that the compositions giving the highest electrical resistivities at those temperatures will give the greatest resistance to puncture; and hence the conclusions cited for the effect of composition on specific resistance will apply to dielectric strength. For high-frequency voltages the compositions showing the lowest power factors can be expected to furnish the greatest resistance to failure. There is practically nothing in the literature to indicate what might be the most desirable composition to withstand impulse voltage or high voltages in the low-temperature zone where disruptive or electrical failure occurs.

Nature of Dielectric Failure in Glass

It has been pointed out that the dielectric strength of glass is affected by the temperature in a peculiar manner. The glass becomes progressively weaker with increasing temperature after a critical temperature is exceeded, whereas below the critical temperature the glass strength remains constant even though the specific resistance changes tremendously. The dielectric strength of glass seems to be a real physical constant of the material when tests are made at ordinary temperature on thin sections. It is argued by some that the strength becomes less as the section increases in thickness, on account of internal heating and the inability, due to the poor thermal conductivity of the glass, to dissipate this internal heat. High-frequency currents heat the glass by reason of dielectric losses and are supposed thus to cause a

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[32] Moon, P. H., and Norcross, A. S., *J. Am. Inst. Elec. Eng.*, **49**, 125 (1930).

lowering of strength by increasing the temperature. On the other hand, there seems to be little indication of a relationship between the specific resistances of glasses or their power factors and the dielectric strength at room temperature. In this respect the data conflict. The original tests of Almy [17] showed no definite connection between the specific resistance and the dielectric strength of the glass. However, electrode edge effect was present in Almy's tests, and hence his results are of little absolute value. Güllner [33] tested eleven glasses among which the resistance varied by a factor of 2000, yet the dielectric strength values varied only by a factor of 2. Hence it can be stated that the initial resistance of the glass apparently has little effect on the dielectric strength of the glass. Inge and Walther, on the other hand, found a parallel effect between breakdown voltage and specific resistance. Rochow found puncture strength to remain constant in a temperature interval that caused a change in the specific resistance by a factor of 4×10^5.

The decrease of strength with increasing frequency of the applied voltage may be a heating effect, or it may be due to the electrical effect of the higher frequencies. So far as one can estimate from the observations, the puncture strength at a frequency of 4.35×10^5 is about the same as that of the glass at a temperature of 200° C. when tested with 50-cycle alternating current.

The failure under impulse voltage is considered to be a purely electrical phenomenon. The exact nature of this type of failure has been the subject of considerable discussion. There are two theories, one of ionization by impact, and the other of an ionization of the atoms by means of the intense fields. Apparently the theoretical voltage required to tear electrons from the atoms is greater than experiment indicates to be the dielectric strength of the material, and hence the latter theory seems to have little experimental justification. The ionization-by-impact theory is more in accord with the facts.

A study of the failures due to marginal discharges and progressive failure of the material gives some positive information on the nature of electrical puncture. These studies favor the ionization-by-impact theory of failure. Partial punctures in glass seem to have been observed first by Du Moncel,[34] who noted the spark from the negative pole of an induction coil intermittently breaking its way through the glass test-piece. Quincke [35] observed a discharge from the positive pole of an induction machine which he stated would at times partially puncture the glass before complete penetration occurred. He made a number of observations on the form of the puncture paths and concluded that the

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[33] Güllner, G., *Arch. Elektrotech.*, **21**, 267 (1928).

[34] Du Moncel, *Fortschr. Physik*, **14**, 488 (1858).

[35] Quincke, G., *Ann. Physik*, **48**, 113 (1915).

discharge was driving gas into the glass. The cracks and strains in the test-piece, to which he ascribed considerable importance, have the appearance, however, of having been caused by contraction of the glass after it was melted by the current following the puncture.

No theory seems to be in entire agreement with all the observed facts. This might possibly be due to the fact that the observations did not include all the possible factors. Attention has been directed to the great effect of electrode edge discharges on the dielectric-strength tests, and the assumption is tacitly made that the experiments in which edge discharges were eliminated give the true dielectric strength of glass; but there is little positive proof that this is the case. It has been shown that many properties of glass, such as electrical resistivity, power factor, and specific gravity, depend upon its past thermal treatment, yet all the experiments cited failed to consider this factor as affecting dielectric strength. The blown glass spheres probably were unannealed and the cover plates and biconcave lenses annealed. Also, glasses contain dissolved gases, often as much as 100 per cent by volume, which may have considerable effect on their dielectric strength.

It is probable that all the measurements have been complicated by the larger effects of some of these unconsidered experimental variables, and that the true strength of glass is considerably higher than the present results indicate it to be. As measured it is purely a point effect, depending upon the field strength at that point and upon the velocity and energy of the bombarding ions. It appears that research directed toward measurement of these other factors would be profitable. So far the attempts have been directed toward their elimination; but there is considerable doubt as to how completely this elimination has been accomplished.

The Dielectric Strength of Thick Sections of Glass

All the work discussed so far has been on thin sections of glass, the majority of the measurements having been made on sections not exceeding 0.25 mm. in thickness. The reason for this is fairly obvious, since attempts were made to avoid electrode edge discharges, and this problem becomes almost insurmountable at the higher voltages required to puncture greater thicknesses. Thick sections, that is, sections several centimeters thick, are readily punctured under oil, but such a test gives no information as to the strength in air, which in the majority of cases is the only condition of practical importance. Perhaps one can safely conclude that if a section only 0.2 mm. thick requires a voltage of 60 kv. to cause puncture, then a section a centimeter or more thick is perfectly safe to use at this voltage so far as puncture is concerned. However, if the voltage gradient in service is such that a pronounced corona is formed, then the question as to the effect of this corona has to be answered. So far this problem seems to have been completely neglected.

It seems worth while, nevertheless, to review the small amount of available information on measurements made on thicker sections of glass.

Moscicki[18] tested under oil a soda-lime glass 2.7 mm. thick and obtained a strength of 142 kv_{max} per cm. Under these conditions of test he found that the square of the puncture voltage was proportional to the thickness. If his results are extrapolated, the strength at one centimeter is 74 kv_{max} per cm., and at 1 in. 118 kv_{max} per in.

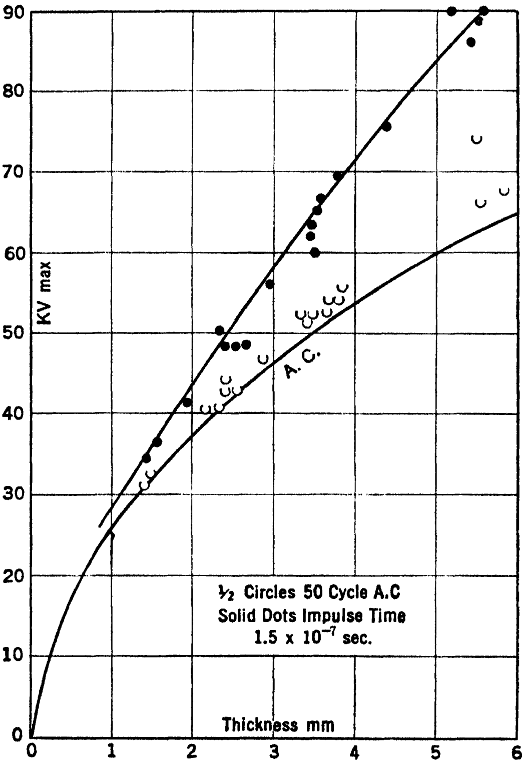

FIGURE XVIII. 14.—Relation between Puncture Voltage and Thickness. After Inge and Walther.

Inge and Walther[36] gave the results of measurements on plate glass tested under oil between 25-mm.-diameter plane disc electrodes with rounded edges. Their measurements were made with impulses of

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[36] Inge, L., and Walther, A., *Arch. Elektrotech.*, 24, 259 (1930).

different duration and with 50-cycle alternating current. Their curve for an impulse time of 1.5×10^{-7} second and for 50 cycles is reproduced in Fig. XVIII. 14.

The same relation between thickness and the square of puncture voltage observed by Moscicki holds approximately for the 50-cycle curve for the interval 2 to 6 mm.; and by extrapolation a strength of 83.5 kv_{max} per cm. is obtained for 1-cm. thickness and 133 kv_{max} per in. for 1-in. thickness. There is no doubt that the strengths of samples 1 cm. and 1 in. thick tested in air would very greatly exceed these values.

The impulse puncture strength under oil is much more nearly proportional to the thickness. The curve in Fig. XVIII. 14 leads to the relation:

$$V = (d/.0135)^{0.727}$$

where d is thickness in millimeters and V is puncture voltage in kilovolts. This gives a dielectric strength of approximately 150 kv. per cm. for 1-cm. thickness and 300 kv. per in. for 1-in. thickness.

There are very few published tests on thick sections with which to make comparisons. Unpublished measurements made in the laboratory of the Corning Glass Works show that dielectric strengths exceeding 150 kv_{max} per cm. have been obtained on samples of Pyrex electrical resistant glass insulators approximately 1 cm. thick, tested under dry oil with 60-cycle a.c. voltage and values about 300 kv_{max} per cm. on 1-in. thicknesses. These higher strengths, which are about twice those found by Inge and Walther, may be due to the different kind of glass used. Tests made in air on similar insulators having thicknesses of only 1 to 2 mm. at the point tested gave puncture strengths 1000 to 1500 kv_{max} per cm., which shows that the strength in air far exceeds the strength under oil. The voltages encountered in these tests were as high as 250 kv_{max}, which was sufficient to cause considerable corona.

Warren [37] gave some data on "Pyrex Glass,"* "Lead Glass," "Lime Glass" and "Soda Glass." It is probable that the "lime glass" and the "soda glass" were of very similar compositions, if they were commercial glasses. His measurements were made in air on samples 50 mils thick (1.27 mm.) most probably with 50-cycle alternating current with results expressed in effective volts. In order to have a comparison with the data previously cited, his results have been changed to kilovolts (maximum) per centimeter and are given in Fig. XVIII. 15. The "Pyrex" showed a strength of 440 kv_{max} per cm. or 1100 $\text{volts}_{\text{max}}$ per mil on pieces 50 mils thick. This is not in agreement with the value of 1000-1500 kv_{max} per cm. obtained in the Corning Glass Works Laboratory on the same glass. In the Corning tests, the insulators were

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[37] Warren, H., *Electrician*, 108, 286 (1932).

* This loose term probably means a Pyrex chemical resistant glass.

carried up to the flashover point at the rate of 80 kv_{max} per minute and held at the flashover voltage for 15 seconds unless puncture occurred in the meantime. The difference between these results and those of Warren must have been caused by the difference in corona action due to the different field distribution.

There seems to be no published information on the impulse strength of thick glass in air; unpublished data furnished by the Corning Glass Works Laboratory show that Pyrex insulators about one-half inch thick have withstood repeated discharges of a "lightning generator" at 1500 kv. The impulse time intervals and wave form are not stated. This gives a value in air of 1200 kv. per cm. without failure, as compared to the value cited above of 150 kv. per cm. for another glass tested in oil. This difference no doubt is due not entirely to the difference between the two glasses, but also to the difference between the effect in oil and in air.

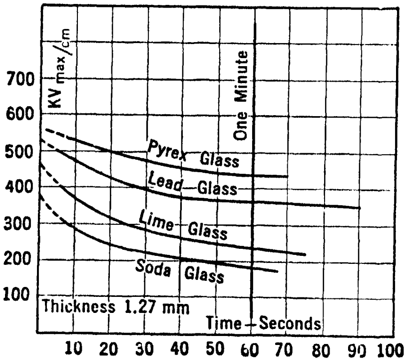

FIGURE XVIII. 15.—Change in Dielectric Strength with Time. After Warren.

The lowering of strength previously mentioned, caused by the heating effects of the conduction current and of high frequencies, was observed only on test samples having very large electrode areas compared to the thickness, a condition favorable to heating both by conduction and by dielectric loss. In practice, where insulators are used with high voltages, the condition is just the reverse. The frequencies are low in the case of power line insulators; and all insulators designed for high-frequency service are designed so as to have very low capacity and large thickness, so that ordinarily there is no danger from either conduction currents or dielectric losses. High-capacity insulators for very high frequencies should be avoided, or else the material should be carefully tested under conditions approximating service requirements, as heating under such conditions might easily lead to failure.

In the case of special service such as is encountered in high-voltage cathode discharge tubes, the impact of discharge on the insulation should be avoided by proper design of the tube or by shielding, as this action may be destructive.

From a consideration of the information discussed, it appears that some glasses, so far as their dielectric properties are concerned, are well adapted to use in commercial insulators. There is no information on the effect of mechanical stress on dielectric strength; but it seems probable that the high dielectric strength of glass offers an ample factor of safety, provided the mechanical stresses do not approach the limit of resistance of the glass.

Chapter XIX

The Magnetic Properties of Glass

The property of glass of interest in connection with magnetic phenomena is that which expresses the amount in which the material resists or opposes the magnetic flux. The total flux, ϕ, in a magnetic circuit is directly proportional to the magneto-motive force, *mmf*, and inversely proportional to the reluctance, R; $\phi = mmf/R$, a relation which is analogous to Ohm's law in electrical circuits. In practice the magnetic flux density, $B = \phi/\text{area}$, is used in place of the total flux, and the magnetizing force per unit length, $H = mmf/l$ in place of the magneto-motive force, which leads to the relation $B = (H/R)(l/A)$, involving the shape factor l/A. In place of the reluctance in the above equation it is customary to use the permeability, μ, defined by $\mu = B/H$, which is a measure of the number of times that a material conducts or aids magnetic flux better than does air (or vacuum). When the permeability is greater than unity, the substance is said to be paramagnetic; when less than unity, diamagnetic. The specific property of the materials in a magnetic circuit may also be expressed in terms of the susceptibility, κ, which is related to the permeability by the relation $\mu = 1 + 4\pi\kappa$. When a substance is placed in a magnetic field it becomes a magnet, and the ratio between the intensity of magnetization, which is a measure of the magnetic moment per unit volume, and the magnetizing force, H, is the susceptibility. For a paramagnetic substance the susceptibility is positive, for a diamagnetic substance, negative.

Experimental Results

Our knowledge of the magnetic susceptibility of glass is due to the work of Koenigsberger[1] who included several glass samples among the numerous solids and liquids which he studied. The results obtained with ten optical glasses from Schott u. Gen. are assembled in Table XIX. 1. In addition the following miscellaneous samples of unknown composition were measured. Several microscope slides were diamagnetic, κ ranging from -0.40 to -0.80×10^{-6}, and some greenish cover slips were weakly paramagnetic, $\kappa = +0.40 \times 10^{-6}$. Cobalt glass was paramagnetic, $\kappa = +2.15 \times 10^{-6}$; "cathedral glass," yellowish green in color, $\kappa = 23.3 \times 10^{-6}$. In some cases the susceptibility showed a small

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[1] Koenigsberger, J., *Ann. Physik Chem.*, **66**, 698 (1899).

change with the field strength as shown by some of the glasses of Table XIX. 1; but such an effect is not the rule. The paramagnetic cobalt and cathedral glasses showed practically no effect of field strength. In general it may be said that glasses free from Fe_2O_3 and Mn_2O_3 are weakly diamagnetic, as is quartz, but that addition of small amounts of these paramagnetic oxides causes the glass itself to become paramagnetic.

TABLE XIX. 1—Magnetic Susceptibility of Some Glasses

Magnetic susceptibility, κ, in units of 10^6 cgs, as function of magnetic field-strength, H, in gausses

After Koenigsberger

No., Table III. 4	κ			No., Table III. 4	κ		
	$H =$ 1350	$H =$ 1800	$H =$ 2200		$H =$ 1350	$H =$ 1800	$H =$ 2200
2	−0.90	−0.90	−0.90	21	−0.93	−0.93	−0.93
*	−0.85	−0.865	−0.885	30	−0.91	−0.92	−0.93
4	−0.93	−0.93	−0.93	31		−0.38	−0.395
15	−0.59	−0.60	−0.607	35	−0.95	−0.95	−0.95
19	−0.78	−0.78	−0.78	41	−1.01	−0.01	−0.01

* Silicate crown, O2161, n_D, 1.5109; SiO_2, 69.15; B_2O_3, 1.0; Na_2O, 6.5; K_2O, 12.0; ZnO, 11.0; As_2O_3, 0.3; MnO_2, 0.05.

Faraday Effect

Faraday [2] found that when polarized light passes through glass in a magnetic field in the direction of the lines of magnetic force, the plane of polarization is rotated. The direction of rotation depends on whether the light is travelling through the glass in a *N-S* or a *S-N* direction; the rotation is doubled if the light is reflected back through the glass. "Faraday's glass," which tarnished in the air so readily as to make it difficult to prepare good surfaces, was a borate flint.

The angle of rotation, α, of the plane of polarization is given by

$$\alpha = CHl$$

in which l is the length of the path; H, the field strength; and C, Verdet's constant.

The Faraday effect has been studied by many observers, some of whom have incidentally used glass. Brace [3] used prisms of "Faraday's glass," $n_D = 1.72$ and 1.76. Most of our knowledge of the Faraday effect in glass is due to duBoise,[4] who measured Verdet's constant for the Schott glasses studied by Rubens (p. 411). The results are given in Table XIX. 2.

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[2] Faraday, M., *Trans. Roy. Soc.* (*London*), **120**, II, 1 (1830).

[3] Brace, W. B., *Ann. Physik Chem.*, **26**, 576 (1885): *Phil. Mag.*, **1**, 464 (1901).

[4] duBoise, H., *Ann. Physik Chem.*, **51**, 547 (1894).

TABLE XIX. 2—Verdet's Constant, C, of Some Glasses

After duBoise

No., Table III. 4	C
12	0.0190
13	0.0234
27	0.0220
28	0.0317
40	0.0442
43	0.0608
45	0.0888
49	0.0163
74	0.0161

Kerr Effect

By the "Kerr effect" is meant the birefringence produced in an isotropic medium by an electric field. It is analogous to the Faraday effect, and was searched for without success by Faraday.

The relation between observed birefringence, or measured path difference d, and potential P, is given by

$$d = Bl\,(P^2/a^2),$$

in which l and d are length and diameter in cm., and B is the Kerr constant for the material. The quantity B is a function of wave-length, and it more than doubled for one glass when λ decreased from 594 to 441 mμ. The "absolute" Kerr constant $K = B\lambda$, is independent of wave-length. Using it, the above equation becomes $\Delta n = K(P^2/a^2)$, in which Δn is the birefringence, and the absolute Kerr constant may be defined as equal to the difference in the two refractive indices for unit potential difference.

Tauern[5] measured the Kerr effect in a number of Schott glasses with the results given in Table XIX. 3. All the glasses which gave measurable results contained lead oxide. A "borosilicate glass containing less PbO, 24%, and some alumina" (O164) gave a small but negative effect, $B = -0.212 \times 10^{-8}$; a "silicate glass with soda and zinc oxide" (O3551) gave $B = 0.207 \times 10^{-8}$; a "borosilicate glass, with potash, soda and zinc oxide" (3439) gave $B = 0.233 \times 10^{-8}$; and three glasses a "borosilicate, alkali-free, with barium oxide and zinc oxide" (2994), a "silicate glass with barium oxide, zinc oxide and potash" (O211), and a "borosilicate glass with potash and soda" (O3832) showed no birefringence.

With glass the Kerr effect is partly masked by electrostriction; if the dielectric constant is increased by pressure, the electric field will compress the glass, producing a measurable change in volume, and resulting in a birefringence superimposed on the true Kerr effect. This effect was

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[5] Tauern, O. D., *Ann. Physik*, **32**, 1064 (1910).

observed by Quincke,[6] and was more accurately studied by Wüllner and Wien,[7] who measured the change in volume produced in spherical and cylindrical condensers. The volume change found was less than that calculated from the elasticity coefficients of the glass; conversely, Young's modulus calculated from electrostriction was about twice that obtained from acoustic measurements, or from compressibility measurements, assuming Poisson's ratio to be 0.25.

Tauern [5] showed that optical path difference produced by electrostriction is given by

$$d = l(P^2/a^2)(KC/8\pi)$$

in which K is dielectric constant, and C is the stress-optical coefficient. The quantity previously measured was the resultant of the mechanical birefringence and that due to the Kerr effect. The "true" Kerr constant, B', is greater than B by $(KC/8\pi)$, and the correction term was calculated by Tauern for a series of glasses similar to those for which C was measured by Pockels (p. 428). The results are given in the second part of Table XIX. 3, in which B is the measured Kerr constant, B' the constant corrected for electrostriction, and K the absolute Kerr constant.

TABLE XIX. 3—Values of Kerr Constant, B; Corrected Kerr Constant, B_{corr}; and Absolute Kerr Constant, K, of Glasses

After Tauern

No., Table III. 4	% PbO	$B\times10^8$	$B_{corr}\times10^8$	$K\times10^{-13}$
20	27.5	0.093		
28	36.3	0.354		
36	43.8	0.595		
42	61.0	0.952		
43	65.5	1.057		
44	71.0	1.275		
19	25.0	−0.12	0	0
25	30.6	0.18	0.293	1.73
40	50.5	0.56	0.669	3.94
46	70	0.901	0.99	5.83
46	80	1.56	1.385	8.1

The results usually obtained in studies of the Kerr effect are undoubtedly complex in their causes, with the extraneous factors at least equal in magnitude to that sought. Guyer,[8] working in the physical laboratory of the Corning Glass Works, and using methods more delicate and freer from interfering complications than those previously employed, could find no indication of a Kerr effect in the borosilicate glasses investigated.

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[6] Quincke, G., *Ann. Physik Chem.*, 10, 161, 187 (1880).

[7] Wüllner, A., and Wien, M., *Ann. Physik*, 9, 1217 (1902).

[8] Guyer, E. M., private communication.

Chapter XX

The Constitution of Glass

Little is known about the constitution of glass, when by that term is meant the details of atomic and molecular arrangement and spacing, and whether or not the atoms or atomic groups are randomly distributed or grouped into assemblies corresponding to definite compounds. Such knowledge has long been available for gases, and in recent years has been obtained for crystals, especially silicate crystals, largely as the result of the researches of W. H. and W. L. Bragg.[1] But there is no such information as to the structure of liquids and the constitution of solutions, primarily because no adequate theoretical foundation exists for building up such knowledge.

The assumption that the constitution of a large number of liquids of a non-polar type, such as benzene, is that of a completely heterogeneous assemblage of simple molecules corresponding to their chemical formula is in harmony with their thermodynamic properties; but thermodynamics is not competent to prove or disprove the correctness of such assumptions. Liquids of a different type, such as water, require further assumptions to explain their properties. The density of water increasing to a maximum at 4° is readily explained with the aid of hypotheses regarding the constitution of water. It is generally admitted that the unusual property-temperature curves of water can be accounted for by the presence in water of three different molecular species. The observed curves can be represented mathematically by putting several variables into the equation; but that the equation so obtained agrees fairly well with the experimental facts is not proof that the assumptions as to molecular species made in introducing the several variables are correct.

At present the whole theory of molecular association in pure liquids is in an unsettled condition. Older concepts, such as that relating molecular association with the variation in free surface energy, as embodied in the rule of Eötvös, Ramsay, and Shields, have been discredited, but as yet the newer methods of quantum mechanics have not provided a concept of the molecular arrangements in liquids of the "associated" type. The problem is under consideration by several investigators, and the suggestive paper of Bernal and Fowler,[2] as well as numerous studies of water by modern methods, indicates that a pure

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[1] Bragg, W. H. and W. L., "The Crystalline State," Bell, London, 1933.

[2] Bernal, J. D., and Fowler, R. H., *J. Chem. Phys.*, 1, 515 (1933).

liquid has a "structure," a statistical preponderance of typical atomic distributions and spacings, with the environment of any one atom changing constantly.

Meager as is the present knowledge of the constitution of pure liquids, still more meager is the knowledge as to solutions. It was observed early by Raoult that in the case of certain liquids, which we now call polar, the change in thermodynamic properties with composition followed a simple law, which was not even approximately followed by other solutions, especially salts in water. Then van't Hoff and Arrhenius introduced the dissociation theory according to which the solutions which do not obey Raoult's law are made to appear to obey it by multiplying the salt concentration by a factor called "the degree of dissociation," derived from speculations on the constitution of the solutions. This fruitful hypothesis has been the inspiration of much experimental work and has served to correlate a multitude of experimental facts; but in its quantitative application it has not been so happy. The simple dilution law of Ostwald is applicable only with solutions too dilute to be of general interest, and none of the many modifications of it has succeeded in explaining the properties of real solutions. An adequate theory of concentrated solutions is still lacking. We cannot speak with assurance on the constitution of an aqueous solution of common salt, and since some glasses are highly concentrated solutions, it is not surprising that the clue to their constitution has not been found. Indeed, it is not unreasonable to hope that the clue to the whole problem of the constitution of concentrated solutions may come from glasses, as these convenient solutions can be studied over a wide range of temperatures, from the region in which they become saturated or supersaturated with respect to one, two or more different phases. At present the knowledge of the variation of certain physical properties with composition in glass-forming systems is more extensive and complete than in any other type of solution.

The physical properties of glass which have been studied over a temperature range exceeding 1000° C. may be discussed in three categories, which may be termed the high-temperature region above the annealing range, the annealing range itself, and the temperature region below the annealing range, especially at ordinary temperature.

Properties at High Temperatures.

The properties to be considered at high temperatures are of two kinds, namely, physical properties of liquids as functions of temperature and composition, and devitrification, which puts an end to the existence of liquid, and ruins the glass. The temperature at which there is equilibrium between the first trace of a crystalline phase and the liquid, known as the liquidus temperature, is the most important constant in connection with the devitrification of glass. Not only does the liquidus temperature change with composition, but also the identity of the first crystalline phase to separate changes, and the entire composition diagram may be subdivided into fields, each of which is characterized by a different primary phase. The phase-equilibrium diagrams for several glass-forming systems have been considered in Chapter II, but the chief feature of interest at present is the fact that such diagrams show that the compounds which separate as primary phases in the ordinary glass-forming systems are characterized either by decomposing before their melting points are reached, or by flat melting point curves.

In the hypothetical case in which a compound melts without dissociation, that is, melts to a liquid containing no representatives of any molecular species other than those which give rise to the crystalline compound, addition of either of the components of the compound will result in a sharp lowering of the melting point, and the two freezing point curves will intersect at an angle at the composition of the compound. Since there is no dissociation, addition of either component will introduce a new molecular species into the liquid, and the resulting freezing point depression will be the same as if some other substance, not a constituent of the compound, had been added. If, on the other hand, dissociation takes place, there will be in the liquid formed by melting the pure compound representatives of the same molecular species as are obtained on adding excess of either component, and the melting point curve will be flat and will have a horizontal tangent at the composition of the compound. Silicates as a whole, and especially all the alkali and alkaline earth silicates with fields near the composition of common glass, are characterized either by incongruent melting points, or by unusually flat melting point curves, both indicative of much dissociation, and it follows that in glass there exists but a small proportion of these compounds. The compound which freezes out on cooling is not necessarily that which is present in greatest amount in the liquid. It is a question of solubility, and that compound whose solubility limit is first reached will be the first to crystallize. In the liquid there will be an equilibrium between the various molecular species, and when one of these is removed by precipitation, reactions will take place with formation of that compound whose concentration has been diminished by its freezing out.

In discussing the problem of the constitution of glass, it is natural to use such expressions as have been used above, "compounds in the liquid," "molecular species"; but it is not easy to attach any definite meaning to such expressions. Probably no one would urge that all the components of a molten glass are present as oxides in mutual "perfect" solution. There undoubtedly is a large amount of combination of these oxides into molecular groupings or compounds, but these groupings probably are not static, but dynamic. "Combination" between the various atoms and atomic groupings results from a more or less complete interlocking of the various fields of force. The haphazard atomic arrangement of a liquid makes improbable the complete saturation of the fields of force in any one-to-one atomic grouping, but indicates rather a sharing of the atomic binding forces over several adjacent atoms. Such diffuse linkages may give rise to representatives of every possible atomic arrangement, and will show a preponderance of those atomic associations which most completely satisfy the potential requirements; but it is doubtful if any more definite picture of compound formation is justifiable.

It is not helpful to speak of "solvation." That merely brings in a new technical term whose meaning in this connection is hazy and indefinite. Solvation consists in the association of molecules or ions of the solution with molecules of the solvent. It is idle to distinguish any one component of a glassy melt as solvent. The word has a meaning only when one constituent is present in preponderant excess, as in a solution of KNO_3 in H_2O at ordinary temperatures. But when that solution is considered near the melting point of KNO_3, where the liquid contains only a small proportion of H_2O, the distinction between solvent and solute has disappeared, as has also any artificial distinction between the process of solution and fusion. Solvation is a descriptive term suggestive of a loose type of chemical combination. But the only type of combination we can logically assume in a complex liquid whose components form dissociating compounds is loose and dynamic, a statistical preponderance of certain molecular types. The proportions of the various possible types will change with temperature and in a continuous manner, but we are unable to identify these types, or to differentiate the various ways of regarding them. Solvation, molecular aggregation and molecular equilibrium are merely expressions indicating that something of an unknown nature is going on in the solution.

The most probable condition at high temperature of a silicate mixture such as glass may be that of a solution containing representatives of all possible "molecular species," in proportions dependent upon composition and temperature, and changing with decreasing temperature in the direction of increasing proportion of the more complex molecular species. The high melting points of orthosilicate compounds and their stability at high temperatures makes it probable that they constitute a large proportion of the molecular species even in trisilicate glasses; and the extensive dissociation of the more complex silicates such as $Na_2O \cdot 3CaO \cdot 6SiO_2$ makes it probable that they exist in much smaller amount than corresponds to stoichiometrical proportions. Even the existence in the liquid of molecules such as $Na_2O \cdot 3CaO \cdot 6SiO_2$ is entirely hypothetical. That such a compound exists in the crystalline state is undoubted; but a crystal is a definite three-dimensional structural identity, and to identify the unknown molecular aggregation which on crystallizing becomes that compound, if any such aggregation exists, as having the composition of the crystalline compound is an extrapolation of our knowledge which, however plausible, is unwarranted. The existence of certain compounds as the stable products of crystallization of a liquid is no evidence that they exist as such in the liquid, and no knowledge we have at present permits the identification of any compounds existing in the liquid state.

Attempts to ascertain the presence of compounds in glass usually take the form of finding departures from a linear relation between the composition and some property of the glass. This procedure is based on the hypothesis that the properties in question (specific volume, refractivity, surface tension, viscosity) are linear functions of composition when no combination takes place between the components, and that when such combination does take place, the properties become linear functions not of the components themselves but of the compounds formed between them. Such an assumption was discarded[3] long ago as untenable for those aqueous solutions which have been most widely studied. Nevertheless, it has been resurrected again and again, sometimes for one property of solutions, sometimes for another. For example, Tammann,[4] from the extensive studies which have been made of the properties of H_2O-SO_3 mixtures, concluded that the viscosity is the only property which indicates in the liquid the presence of compounds known from the freezing point curves. In a later study[5] of all available data from other systems, he found eight cases in which compounds were indicated by maxima on both the viscosity and the freezing point curves; two cases in which one compound was indicated by viscosity data, although other compounds in the same system were not indicated; eleven cases in which the maximum was at a different composition from that of the compound; seventeen cases in which there was a maximum in the viscosity curve, but no compound; six cases in which the viscosity curve had no maximum, but was above the line joining the viscosity of the two components, and a compound was shown by the freezing point curve; three cases in which the continuous viscosity curve was below the line joining the viscosities of the two components, and a compound

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[3] See the controversy arising out of Mendeléeff's "theory of solutions," based on the inference of the existence of water-soluble compounds from the density curve of the binary mixtures. Mendeléeff, D., *J. Chem. Soc.*, **51**, 778 (1887); Pickering, S. U., *ibid.*, **57**, 64, 331 (1890); *Phil. Mag.* (*5*), **29**, 427 (1890); "Watt's Dictionary of Chemistry," article on "Solutions," ii (1894); Crompton, H., *J. Chem. Soc.*, **53**, 116 (1888); Arrhenius, S., *Phil. Mag.* (*5*), **28**, 30 (1889); Hayes, E. H., *ibid.* (*5*), **32**, 99 (1891); Rücker, A. W., *ibid* (*5*), **32**, 304 (1891); Lupton, S., *ibid.* (*5*), **31**, 418 (1891).

[4] Tammann, G., *Z. anorg. allgem. Chem.*, **161**, 363 (1927).

[5] Tammann, G., and Pillsbury, M. E., *Z. anorg. allgem. Chem.*, **172**, 243 (1928).

was known; and seven cases in which there was a maximum on the viscosity curve, but the melting point curve showed only a eutectic. Later he[6] found a case ($CaO \cdot SiO_2$) in which there was a minimum on the viscosity curve at the composition of the compound, but that has since been disproved.[7] Evidently the viscosity is a frail reed on which to base an argument on the existence of compounds in a liquid phase.

In spite of the accumulation of an enormous amount of data, we have not yet any intimation of an hypothesis which will enable us to predict the heterogeneous equilibrium from the properties of a homogeneous equilibrium. To be sure, by applying laws of so-called ideal solutions to exceptional binary mixtures, the freezing point curves of the two components can be calculated to a reasonable degree of approximation, and from their intersection the eutectic composition and temperature can be obtained. But in the great majority of cases, without exception in all cases resembling silicate mixtures, such a calculation is not approximately fulfilled. In no case have we any intimation as to why a compound is formed. From no theoretical knowledge available today could one predict that a compound of the composition $K_2O \cdot 4SiO_2$ would be present in the system K_2O-SiO_2, and no similar compound in the system Na_2O-SiO_2; or that lithium disilicate would have an incongruent melting points, although sodium and potassium disilicates have congruent melting points. The prediction of the heterogeneous equilibrium from the properties of the components of the homogeneous equilibrium, a fundamental objective of theoretical chemistry, is far from our capabilities at the present time, and there is no known relationship between the properties of a solution and of the substances which form from it on completion of the process of crystallization.

The lack of correlation between the properties of the liquid at high temperature and the phase equilibrium diagram is well illustrated by Figs. V. 3, 4, and 5, in which are represented the lines of equal viscosity in the system Na_2O-CaO-SiO_2 at various temperatures, as determined by Washburn, Shelton, and Libman,[8] together with the boundaries of the liquid[9] at the same temperature. Within the restricted area formed by the liquid boundaries, the liquid alone is stable; outside this region the melt at equilibrium should consist of crystals and liquid. Similarly, Fig. VII. 5 shows the change of surface tension with composition, and here again it is evident that the reactions which should take place, but do not, are without effect on the viscosity.

The vaporization of alkali from an alkali oxide-silica glass has

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[6] Tammann, G., *Z. anorg. allgem. Chem.*, **199**, 117 (1931).

[7] Heidtkamp, G., and Endell, K., *Glastech. Ber.*, **14**, 89 (1936).

[8] Washburn, E. W., Shelton, G. R., and Libman, E. E., *Univ. Ill. Eng. Expt. Sta. Bull.*, **140**, (1924).

[9] Morey, G. W., and Bowen, N. L., *J. Soc. Glass Tech.*, **9**, 226 (1925).

been considered[10] to give evidence of the existence of compounds in glass. The evidence was discussed by Morey,[11] who concluded:

"It is evident that the conclusions quoted are not justified by the experimental results on which they are founded, but even more can be said. Although we cannot make the categorical statement that in a system such as this there can be no discontinuities in such properties as the specific volume or the viscosity, we can be assured that the vapor pressure of any component from such a continuous series of liquids cannot be discontinuous, but must be a continuous function of the composition." Preston and Turner[12] objected to Morey's conclusions, and their objections were considered and rejected by Morey.[13]

Properties at Annealing Temperatures

The various theories of the constitution of glass based on studies in and near the "annealing range" represent an entirely different point of view from those at either higher or lower temperatures, and many of them suggest fundamental changes in our views as to the nature of glass. They are based on a large number of observations by many experimenters indicating that when the change of physical properties with temperature is measured in the annealing range, a more or less well marked discontinuity becomes apparent.

The first observation of this type was that of Day and Allen,[14] "On every occasion when borax glass was heated rapidly, either powdered or in the solid block, a slight but persistent absorption of heat appeared in the same region (490° to 500°) and continued over some 20°, after which the original rate of heating returned." A similar effect was found by So,[15] and later studied extensively by Tool[16] and his colleagues at the Bureau of Standards. Other studies at the Bureau[17] established the fact that the thermal dilatation of glass showed an abnormal increase at the same temperature, and that the properties[18] of glass were altered by variations in the heat treatment in the same temperature region. Schönborn[19] found that the change with temperature of the electrical

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[10] I. Alkali-lead oxide-silica glass. Preston, E., and Turner, W. E. S., *J. Soc. Glass Tech.*, **16**, 219 (1932); II. Sodium silicate-silica glasses. Preston and Turner, *ibid.*, **16**, 331 (1932); III. Potassium oxide-silica glasses. Preston and Turner, *ibid.*, **17**, 122 (1933).

[11] Morey, G. W., *J. Am. Ceram. Soc.*, **17**, 315 (1934).

[12] Preston, E., and Turner, W. E. S., *J. Am. Ceram. Soc.*, **18**, 170 (1935).

[13] Morey, G. W., *J. Am. Ceram. Soc.*, **18**, 173 (1935).

[14] Day, A. L., and Allen, E. T., *Carnegie Inst. Wash. Pub.*, **31**, 34 (1905).

[15] So, M., *Proc. Tokyo Math. Phys. Soc.*, **9**, 426 (1918).

[16] Tool, A. Q., and Eichlin, C. G., *J. Optical Soc. Am.*, **4**, 340 (1920); Tool, A. Q., and Valasek, J., *Bur. Standards Sci. Papers*, **358** (1920); Tool, A. Q., and Eichlin, C. G., *J. Am. Ceram. Soc.*, **14**, 276 (1931).

[17] Peters, C. G., and Cragoe, C. H., *J. Optical Soc. Am.*, **4**, 105 (1920).

[18] Peters, C. G., *Bur. Standards Sci. Papers*, **521**, (1926); Tilton, L. W., Finn, A. N., and Tool, A. Q., *Bur. Standards Sci. Papers*, **572** (1928); Tool, A. Q., Lloyd, D. B., and Merritt, G. E., *Bur. Standards J. Research*, **5**, 627 (1930).

[19] Schönborn, H., *Sprechsaal*, **61**, 99 (1928).

resistance of glass could be represented by two straight lines of the form

$$\log W = (A/T) + B,$$

with an intersection at about the upper limit of the "critical range," as determined by expansivity measurements. Similar results were obtained by Fulda.[20] These and similar studies are mentioned in the appropriate chapters.

One of the first explanations of these observations was that of Lebedeff,[21] according to whose hypothesis, "glass was supposed to contain very minute quartz crystals, which probably contained other substances in solid solution, and the function of annealing appeared to be not so much the removal of stress as the attaining of complete polymorphic equilibrium." Such an hypothesis is, of course, theoretically untenable, since it assumes carrying over into the liquid state a phase change characteristic of one of the crystalline species of silica, and it is experimentally confuted by the fact that the same type of discontinuity is found not only with silicate glasses, but also with phosphate, borate and organic glasses.[22] Indeed, it probably is a characteristic of all liquids which have reached a viscosity of 10^{14} poises or greater.

The evidence of several observers, tending to establish a discontinuity in the change of properties of glass with temperature, has been summarized and discussed by Berger, whose interpretation of the experimental data is different from that here adopted. Berger[23] stated: "But in a small temperature range, or more exactly, at a temperature point, the temperature coefficients of the properties become discontinuous. . . . It is noteworthy that in the case of noncrystalline freezing, all property curves break at the transformation point T_g, the temperature coefficients undergoing sudden changes at this point. . . . The transformation point represents the boundary temperature between viscous and brittle glass, at which boundary the property-temperature coefficients more or less suddenly change." Simon[24] had a similar interpretation, differing mainly in phraseology. He considered that above the transition temperature the material is an undercooled liquid in internal thermodynamic equilibrium; below the transition, a glass, not in internal thermodynamic equilibrium. To a certain extent, this is correct; the attainment of inner thermodynamic equilbrium becomes increasingly time-consuming as viscosity increases, and the lack of equilibrium characterizes glass in an "unstabilized" condition. But Simon, as well as Berger, accepted erroneously the reality and uniqueness of the "transition temperature."

[20] Fulda, M., *Sprechsaal*, **60**, 769, 789. 810, 831, 853 (1927).

[21] Lebedeff,- A. A., *Trans. Optical Inst. Petrograd*, 2, No. 10 (1921); *J. Soc. Glass Tech., Abs.*, **6**, 110 (1922).

[22] Samsoen, M., *Compt. rend.*, **182**, 517 (1926); *J. Soc. Glass Tech., Abs.*, **10**, 168 (1926).

[23] Berger, E., *J. Am. Ceram. Soc.*, **15**, 647 (1932). In this paper are given references to earlier papers by Berger, and numerous other references.

[24] Simon, F., *Z. anorg. allgem. Chem.*, **203**, 219 (1931).

The hypothesis of a transition temperature in glass, above which it is a liquid, below which a solid or a fourth state of matter, has from the beginning been unacceptable to many persons. Tool and Hill,[25] in a paper contributed to a Symposium on the Constitution of Glass held by the Society of Glass Technology in 1925, summarized their views as follows: ". . . under proper cooling conditions, certain processes or reactions practically reversible without drastic treatment and involving some or all of the constituent molecules of a glass shall advance in such a way that other possible and disturbing processes often associated with cooling and with treatments at temperatures above the annealing range are prevented. A consideration of the above conclusions indicates that . . . the condition of a glass . . . at ordinary temperatures may be considered as under-cooled not alone with regard to the process of crystallization, usually known as the true solidification, but also with respect to the completion of many processes normal to the vitreous condition. . . . It has been shown that some of these at least advance and retrogress as the heat treatment is changed and that as a consequence certain properties are modified by altering the effective heat treatment. . . . The character of the processes and the rate at which they advance will change as the glass cools, and when it is held at any given temperature, this rate should decrease with time until a state of practical equilibrium becomes established after a period the length of which depends on the temperature. In those ranges in which glass is easily deformable, this period should be relatively short and in the upper part of the annealing range will not exceed an hour, perhaps, but not far below the lower part it may approach a duration of months." Tool and Hill evidently considered that the processes which take place in the annealing range are continuous. Similar views were expressed by Morey and Bowen [26] in a contribution to the same Symposium. Koerner and Salmang [27] showed by dilatometric measurements that the position of the transition temperature is dependent on the heating rate, and considered it solely an undercooling or overheating phenomenon. Annealed glass flows below the transformation temperature.

Further researches have confirmed the view of the continuity of the changes which take place in glass in the annealing range, and even down to lower temperatures. The discussion by Littleton [28] established this in an adequate manner. The evidence of a "change in state" obtained from measurements of thermal expansion, viscosity and electrical conductivity was critically discussed with the aid of new measurements of electrical conductivity and viscosity; and the conclusion was

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[25] Tool, A. Q., and Hill, E. E., *J. Soc. Glass Tech.*, **9**, 185 (1925).

[26] Morey, G. W., and Bowen, N. L., *J. Soc. Glass Tech.*, **9**, 226, 260 (1925).

[27] Koerner, O., and Salmang, H., *Z. anorg. allgem. Chem.*, **199**, 285 (1931).

[28] Littleton, J. T., *Ind. Eng. Chem.*, **25**, 748 (1933).

reached that "there are no critical temperatures in the properties of glasses. There is a change of some sort, possibly in degree of dissociation or a molecular aggregation which occurs at all temperatures until a stabilization has taken place." In other words, the properties of glass change with temperature, at a rate which is dependent on the temperature. At higher temperatures this change takes place rapidly, so that the properties as measured represent the equilibrium values of those properties at the temperature in question. As the temperature is lowered, the rate at which these equilibrium values are reached diminishes, until well below the annealing range it is necessary to hold the glass an impracticable length of time for it to become stabilized in the equilibrium condition. But that even far below the annealing range continuous change does take place has been shown by several observers. Morey and Merwin [29] found that the attainment of an equilibrium or maximum density required an increasingly long time as the temperature was lowered below the annealing range, but that when the heat treatment was prolonged for several months, the glasses did change in density, reaching a value higher than the maximum which would have been reached at the ordinary annealing temperature. Lillie [30] showed that in the lower portion of the annealing range several days are required to reach the equilibrium viscosity, which may be approached from either lower or higher temperatures. At temperatures at which the equilibrium value of the viscosity was 3.38×10^{15} poises, the viscosity in three days had increased from an initial value of 0.2×10^{15} to 2.6×10^{15}, indicating that a considerably longer time would have been required for the glass to reach a state of equilibrium in regard to viscosity. Morey and Warren [31] studied the rate of annealing of Pyrex chemical resistant glass at a temperature at which its viscosity was of the order of 10^{19} poises. The rate of loss of strain at first decreased and did not become constant until after six weeks, after which it remained practically constant for 22 months. The later results of Lillie [32] make it probable that even in two years the glass had not become completely stabilized.

Littleton and Wetmore [33] made a careful study of the rate of stabilization of glass and the change in electrical conductivity as stabilization proceeds, which is considered in detail on page 462. This study confirmed the conclusion that the curve of conductivity against temperature shows no break with stabilized glasses.

The conclusion seems inescapable that there is no discontinuity of properties in the annealing range, or even well below that range, provided the measurements are made on glasses which have been held

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[29] Morey, G. W., and Merwin, H. E., *J. Optical Soc. Am.*, **22**, 632 (1932).

[30] Lillie, H. R., *J. Am. Ceram. Soc.*, **16**, 619 (1933).

[31] Morey, G. W., and Warren, B. E., *Ind. Eng. Chem.*, **27**, 966 (1935).

[32] Lillie, H. R., *J. Am. Ceram. Soc.*, **19**, 45 (1936).

[33] Littleton, J. T., and Wetmore, W. L., *J. Am. Ceram. Soc.*, **19**, 243 (1936).

at constant temperature long enough for the equilibrium values to be attained. There is no justification for assigning any particular temperature as the boundary line between "viscous" and "brittle" glass, or a boundary between the "undercooled liquid" and the "amorphous solid" condition. It should be emphasized that discontinuities found from measurements made with continuously changing temperature on properties which not only change with temperature, but also require considerable time to reach an equilibrium value, cannot be admitted as evidence of a real change in the condition of the glass. Nor is it to be expected that slight changes in the rate of heating will greatly modify such discontinuities. The fact that a discontinuity is observed at all with continuous heating indicates that a stored-up lag in the glass is suddenly released, and slight modifications in the heating rate can but slightly modify the temperature at which the release takes place. The fact that such slight changes in the heating rate in the region of high viscosity only slightly modify the temperature of such apparent discontinuities is not evidence of their reality. When it is considered that in the lower portion of the annealing range weeks or months are required to "stabilize" the glass, it is evident that measurements made with changing temperature are not pertinent to the question, and experimenters are urged to make their measurements on glasses in an equilibrium condition, and to show that such a condition has been reached, as was done by Lillie.

All the hitherto puzzling effects obtained with glass in the annealing range may be explained completely on the assumption that the condition of the glass changes continuously with temperature, in the direction of an increasing density and a decreasing inter-atomic distance as the temperature is lowered, and that the rate at which the equilibrium or stabilized condition is reached decreases rapidly with decreasing temperature, so that an increasingly long time is required for stabilization as the temperature is lowered. When the glass is cooled without continuous stabilization, a condition becomes frozen-in which is characteristic of some temperatures passed through on cooling. This change probably is one consisting only in diminishing the interatomic distances, and not in the major atomic movements necessary to form new atomic arrangements.

When the glass is heated, it changes in properties both as the result of change in the temperature alone, and as a result of its departure from the equilibrium condition. When the temperature is raised quickly enough, the movement toward stabilization may overshadow the effect of temperature alone, and thus produce an apparent discontinuity, the temperature of which will depend on the previous thermal history and the rate of heating. The process in no way resembles the transition from one crystalline form to another, and no discontinuity appears when the heating is slow enough for the properties of the glass to reach constant values at each temperature.

The importance of the transition to the crystalline condition should not be overlooked in this discussion. It has been often implied, and sometimes stated, that below the transition temperature the glass is solid, molecular movement is impossible, and devitrification cannot take place. Berger even affirmed that the crystalline phase becomes unstable with respect to the glass at a temperature well below the transition temperature. No evidence is given for this extraordinary view; nevertheless Zwicky[34] has assumed its truth in a discussion of the crystalline state. As a matter of fact, most glasses can be crystallized without difficulty below the transition temperature. Several examples were mentioned incidentally by Morey and Merwin.[29] Morey has crystallized $Na_2O \cdot SiO_2$ glass by long heating at 200°. Some glasses, such as those made by rapid cooling of Sb_2O_3 or selenium, are said to crystallize spontaneously at room temperature, even though they are hard and very brittle glasses. Wietzel,[35] testing the "third law" of thermodynamics for fused and crystalline silica, concluded that the entropy of the fused was greater than that of the crystalline silica at liquid hydrogen temperatures. Gibson and Giauque[36] found that the entropy of glycerin in the condition of an undercooled liquid exceeded that in the crystalline condition by 5.6 cal. per degree per mole at 70° K. There is no evidence in support of the improbable hypothesis that at lower temperatures the glassy form becomes more stable than the crystalline, and abundant evidence exists, and can readily be confirmed, that devitrification may take place far below the so-called transition temperature.

Properties at Ordinary Temperatures

Two methods have been applied to the elucidation of the constitution of glass at ordinary temperatures. In any such study it must be remembered that the glass represents a rigid material which has cooled with continuously increasing viscosity from above its crystallizing temperature, first through a region in which its properties quickly take on the values characteristic of equilibrium, then through a region in which an increasingly long time is required for the equilibrium to be reached, so that, even though the glass may have been "annealed," its properties at ordinary temperatures represent the frozen-in equilibrium corresponding to some, usually unknown, higher temperature. If glasses are to be compared, they should be in some comparable state, but what that state should be is unknown. It has been shown by many authors that

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[34] Zwicky, F., *Proc. Nat. Acad. Sci. U. S.*, **17**, 524 (1931).

[35] Wietzel, R., *Z. anorg. allgem. Chem.*, **116**, 71 (1921).

[36] Gibson, G. E., and Giauque, W. F., *J. Am. Chem. Soc.*, **45**, 93 (1923).

the properties of the cooled glasses are dependent on their thermal history, and it is not sufficient merely to anneal to remove mechanical strain. Such strain does exist in glass quickly cooled, but as Adams[37] has shown, it alone can have no effect on the density, and presumably not on such other properties as the refractive index or the electrical conductivity. The real differences found are the result of differences in heat treatment, and many of the differences between the results of recent observers are to be ascribed to differences in the heat treatments adopted by them. We have no reason for saying that any one of these treatments is erroneous, or that any other is the correct one. Such positive statements must wait until we know what are the fundamental reasons for the effects observed, and then what is the comparable condition at which we should aim.

Many experimenters have considered that the presence of compounds in glass at ordinary temperatures could be shown by discontinuities in the property-composition curves. Specific volume is the favorite property for the support of these speculations, with refractive index of specific refractivity the second choice. The validity of the fundamental assumption underlying this treatment has already been discussed; and whether or not the conclusions reached appear valid, it must be admitted that, for deviation from linear relationship between composition and property to be proof of compound formation, it is necessary that the experimental results be adequate both in number and precision, and that their representation by the broken curves of the compound theory be markedly superior to any other mode of representation. It is safe to say that as the number and precision of the measurements have been increased, their representation by broken curves, as opposed to continuous curves, has become increasingly improbable. For example, consider the specific volume of the Na_2O-SiO_2 and the Na_2O-CaO-SiO_2 glasses. The earlier measurements were made on glasses which had not been analyzed, which were of uncertain composition, and had not been heat-treated or annealed. In some cases measurements were made on fire-polished surfaces. Deductions drawn from these earlier measurements may be dismissed from consideration. Later Turner,[38] making use of the density measurements of Peddle,[39] expressed the specific volume by two straight lines intersecting at the composition of $Na_2O \cdot 2SiO_2$. The measurements were made on glasses which were not analyzed, but the compositions were calculated from the proportions of the ingredients melted. Winks and Turner[40] made more accurate measurements on a more extensive series of analyzed glasses, and found

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[37] Adams, L. H., *J. Franklin Inst.*, **216**, 39 (1933).

[38] Turner, W. E. S., *J. Soc. Glass Tech.*, **9**, 147 (1925).

[39] Peddle, C. J., *J. Soc. Glass Tech.*, **4**, 1 (1920).

[40] Winks, F., and Turner, W. E. S., *J. Soc. Glass Tech.*, **15**, 185 (1931).

that the results were better expressed by a continuous curve. Glaze, Young, and Finn[41] made accurate measurements on glasses of known composition in the binary system Na_2O-SiO_2 and also in the ternary system Na_2O-CaO-SiO_2, and they concluded that in the binary glasses the results were better expressed by four straight lines, implying the assumption of three silicate compounds, $2Na_2O \cdot 3SiO_2$, $Na_2O \cdot 2SiO_2$, and $Na_2O \cdot 3SiO_2$, of which $2Na_2O \cdot 3SiO_2$ and $Na_2O \cdot 3SiO_2$ are entirely hypothetical. It is evident from an inspection of their curves that this interpretation is not a necessary one, and re-plotting their results confirms this conclusion.[42] They abandoned the hypothesis of compound formation in presenting their results for the ternary system Na_2O-CaO-SiO_2.

The most extensive group of results on this system is that of Morey and Merwin,[29] who measured glasses well distributed over the entire ternary system from mixtures intermediate between the orthosilicate and the metasilicate ratios to SiO_2. Their results for density and refractive index and the conclusions drawn therefrom are given in Chapters X and XVI. They also calculated the specific refractivity of all their glasses by four different formulas (Fig. XVI. 4), and concluded that specific refractivity is roughly additive, and the departures from the additive relationship are not such as would be expected from any specific effect of compound formation.

The results of the many observers on the physical properties of glass at ordinary temperatures indicate that no justification exists for an assertion that definite compounds exist in, and determine the properties of, glass.[43]

A second method which has been applied to the study of the constitution of glass at low temperatures is that of x-rays. Wyckoff and Morey[44] obtained x-ray diffraction patterns from a number of glasses in the ternary system Na_2O-CaO-SiO_2, and also the patterns of crystalline compounds in the same system,[45] and established the fact that the type of pattern obtained depended on the composition of the glass. In some cases the broad band patterns typical of liquids were obtained, although with other compositions the narrower bands were as sharp as those obtained from crystals of colloidal dimensions. In glasses high in SiO_2 these bands corresponded only roughly to the strong band from cristobalite crystals. Attempts to prove correspondence between the glass pattern and that of the crystalline compound which should separate, failed. For example, $Na_2O \cdot 2CaO \cdot 3SiO_2$ is a definite compound whose

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[41] Glaze, F. W., Young, J. C., and Finn, A. N., *Bur. Standards J. Research*, **9**, 799 (1932).

[42] Preston, E., and Turner, W. E. S., *J. Am. Ceram. Soc.*, **17**, 26 (1934).

[43] Preston, E., and Turner, W. E. S., *J. Soc. Glass Tech.*, **20**, 144 (1936). Preston, E, and Seddon, E., *ibid.*, **21**, 123 (1937). Heidtkamp, G., and Endell, K., *ibid.*, **21**, 263 (1937).

[44] Wyckoff, R. W. G., and Morey, G. W., *J. Soc. Glass Tech.*, **9**, 265 (1925).

[45] Wyckoff, R. W. G., and Morey, G. W., *Am. J. Sci.*, **12**, 419 (1926).

structure has been determined approximately, and a glass of this composition gives a diffuse line pattern. When the glass was crystallized slowly, the diffuse lines did not sharpen into the lines characteristic of the crystal, but instead a new pattern developed, and the patterns due to the glass and to the crystal were not the same.[46] That the glass was crystallizing could be seen with the eye before it could be detected on the x-ray plate.

Parmelee, Clark, and Badger[47] concluded that the diffuse ring type of pattern indicates incipient crystal formation. Clark and Amberg[48] concluded that the SiO_2 molecule is the unit of structure in SiO_2 glass, the molecules being arranged end to end in long chains, the chains grouped into bundles. Some details of their experimental work have not been confirmed. Randall, Rooksby, and Cooper[49] obtained essentially the same results as previous workers, but they drew far-reaching conclusions from them. From the limited resemblance of the patterns of amorphous precipitated silica and of silica glass to that of high cristobalite, they said: "It follows, then, that there is little structural difference between these two forms of silica. In this sense the workers who hold to the 'amorphous' theory of glasses are correct. The essential point is that the term 'amorphous' has no meaning. The difference between the crystalline state, on the one hand, and the 'vitreous' and 'amorphous' on the other is one of degree, not of kind." In the discussion[50] Randall stated: "In ordinary vitreous silica he thought it quite reasonable to say there must be some 80% of cristobalite." The views quoted in this paragraph have not been confirmed by the more recent work.

Zachariasen[51] published an interesting discussion of the atomic arrangements in glass. He said: ". . . the atoms in glass must form an extended three-dimensional network. From the results of x-ray diffraction experiments it follows, however, that this network is not periodic and symmetrical as in crystals. Yet it is not entirely random due to the fact that the internuclear distances do not sink below a given minimum value. All atomic distances are for this reason not entirely probable, and x-ray patterns of the type observed will be a direct consequence. If we make use of crystal structure terminology, we may say that the network in glass is characterized by an infinitely large unit cell containing an infinite number of atoms. Because of the lack of periodicity no two of the atoms are structurally equivalent . . ." This picture of the

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[46] Morey, G. W., *J. Am. Ceram. Soc.*, **17**, 315 (1934).

[47] Parmelee, C. W., Clark, G. L., and Badger, A. E., *J. Soc. Glass Tech.*, **13**, 285 (1929).

[48] Clark, G. L., and Amberg, C. R., *J. Soc. Glass Tech.*, **13**, 290 (1929).

[49] Randall, J. T., Rooksby, H. P., and Cooper, B. S., *J. Soc. Glass Tech.*, **14**, 219 (1930); *ibid.*, **15**, 54 (1931).

[50] Randall, J. T., Rooksby, H. P., and Cooper, B. S., *J. Soc. Glass Tech.*, **15**, 54 (1931).

[51] Zachariasen, W. H., *J. Am. Chem. Soc.*, **54**, 3841 (1932).

structure of glass, which seems much more probable than that given by Randall, Rooksby, and Cooper, makes a fundamental distinction between the three-dimensional ordered periodicity of a crystal and the limited order in a glass. The picture is that of an undercooled liquid in which the great increase in viscosity has rendered permanent the ever-shifting order in a liquid. As mentioned before, there is an increasing amount of evidence that liquids possess a structure: that in nonpolar liquids the tendency is for a structure the unit of which is molecular (such as the parallel orientation of the paraffin hydrocarbons), and that in polar liquids the structure is atomic. All liquids, however, definitely lack three-dimensional periodicity and are characterized by continuous change. To bring in again the anology of water, the x-ray diffraction patterns of liquid water at temperatures from 1.5° to 80° C., given by Warren [52] from the unpublished work of Morgan, indicate as definite a structure as the x-ray diffraction patterns obtained with glasses.

Warren[53] has presented a definite picture of the structure of silica glass, a structure based primarily on experimental results, and agreeing with that deduced by Zachariasen. He also found that the x-ray patterns of both vitreous silica and Pyrex chemical resistant glass show a single broad diffraction ring whose maximum corresponds to a value of 4.32 Å for the spacing in silica. Warren discussed the two possible explanations of the observed diffraction patterns, and rejected that explanation which ascribes the pattern to crystallites of cristobalite; the rejection was based on discrepancies in the calculated spacing, in the volume-temperature relations, and the behavior of the material on heat treatment. The accepted hypothesis is based on scattering from a noncrystalline random network, in which each silicon is tetrahedrally surrounded by four oxygens, and each oxygen is shared by two tetrahedral groups. The nearest neighbors of any tetrahedral group are approximately fixed in position, but beyond this the spacing is wholly random. The x-ray spacing from such a random network was calculated, using Zernicke and Prins' method of treating the problem of diffraction in liquids, with satisfactory agreement between the observed and the calculated results.

In a more recent discussion Warren [52] said:

"The x-ray results are completely explained by picturing glassy silica as a random network in which each silicon is tetrahedrally surrounded by four oxygens, each oxygen bonded to two silicons, the two bonds to an oxygen being roughly diametrically opposite. The orientation of one tetrahedral group with respect to a neighboring group about the connecting Si—O—Si bond can be practically random. This is the simplest picture of silica glass free from all specialized assumptions,

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[52] Warren, B. E., *J. Applied Phys.*, **8**, 645 (1937).

[53] Warren, B. E., *Z. Krist.*, **86**, 349 (1933).

which will completely explain the x-ray diffraction pattern. There is a definite scheme of structure involved. Each atom has a definite number of nearest neighbors at a definite distance, but no unit of structure repeats itself identically at regular intervals in three dimensions; and hence the material is not crystalline. This is essentially the picture of an oxide glass at which Zachariasen arrived from consideration of the chemical composition." Fig. XX. 1 illustrates schematically in two dimensions the irregular structure of a glass as distinguished from the regularly repeating structure of a crystal.

Warren pointed out that "the strongest ring in the cristobalite pattern [Fig. XX. 2] comes at very nearly the position of the first broad peak in the vitreous silica pattern, and since the breadth of the lines on a powdered crystalline pattern increases continuously with decreasing size of crystalline particles, it is evident that if one postulates in vitreous silica cristobalite crystals sufficiently small, the strong peak of cristobalite would broaden out to give the appearance of the vitreous pattern." However, calculation shows that the average dimension of the cristobalite particles would have to be 7.7 Å, and "Since the edge of the unit cell of cristobalite is about 7.0 Å, we are forced to postulate cristobalite crystals comprising scarcely more than one unit cell in order to explain the observed peak width. Since the essence of the idea of crystallinity is regular repetition it becomes decidedly artificial and formal to extend the term crystal to cover so small an aggregation of atoms."

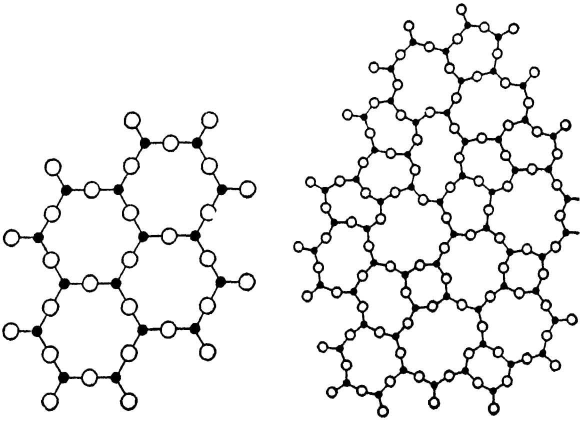

FIGURE XX. 1.—Schematic Representation in Two Dimensions of the Difference between the Structure of a Crystal (Left) and a Glass (Right). After Zachariasen.

A commercial silica gel (Fig. XX. 2) gave an x-ray diffraction pattern with a main peak in about the same position as in silica glass, but with a strong small-angle scattering which was completely absent in the glass. Small-angle scattering is due to large-scale inhomogeneities in the sample, and with the silica gel it is primarily due to the existence of discrete particles with voids between them. Further consideration of small-angle scattering led to the conclusion:

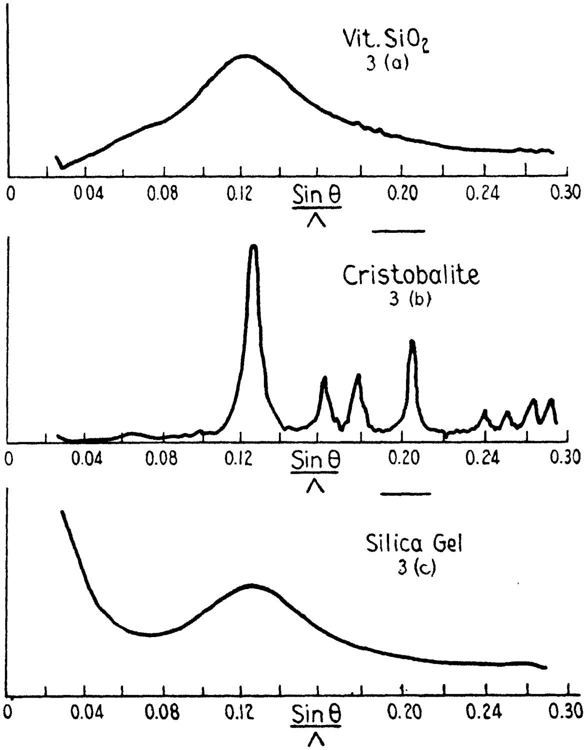

FIGURE XX. 2.—Microphotometric Records of X-Ray Diffraction Patterns of (a) Vitreous Silica, (b) Cristobalite, and (c) Dried Commercial Silica Gel. After Warren.

"Considering the small size of the crystallites and the relatively thick layer of non-crystalline continuous network necessary to bond together continuously two separate crystals, one is forced to conclude that even though he postulates cristobalite crystals in the glass, only a small fraction of the material could be in this form.

"Although a number of workers have tried to explain the x-ray diffraction patterns of glass as due to extremely small crystals, the objections which have been brought out in this discussion appear much too severe to accept this picture of the glassy state. The crystal-

> line theory leads to a size of crystalline particle so small that to call it a crystal is stretching the term so far that it ceases to have any definite meaning. The absence of small-angle scattering means that the glass is a continuous medium with no discrete particles or breaks in the scheme of bonding. Therefore even if one assumes tiny cristobalite crystals in the glassy silica, only a fraction of the material could be in this form. On the basis of the crystallite theory one is still left with the problem of explaining an extremely small and approximately constant particle size in order to explain the peak width. . . . glass is a liquid of extremely high viscosity in which the atoms are too tightly tied together in an irregular network to allow the breaking up and reforming necessary for crystallization.
>
> "The term random network has been suggested for this picture of the glassy state. There is a definite scheme of coördination and a continuous system of bonding with no breaks or discrete particles, and yet no unit of structure repeats itself identically at regular intervals so that the material is noncrystalline. This is the simplest picture of the glassy state which will explain completely the x-ray diffraction results. In addition it is a picture which differs sufficiently from the picture of a crystalline material to allow an understanding of the very definite differences which do exist between the glassy and crystalline states."

Warren and Loring[54] studied a series of glasses in the system Na_2O-SiO_2, and Warren and Biscoe[55] studied the same glasses, using improved experimental methods and treating the results by the method of Fourier analysis. The resulting set of curves showing the relation between radial distribution of atoms surrounding any given atom is reproduced as Fig. XX. 3. The first peak corresponds to the interatomic distance between silicon and oxygen atoms, which in all silicates, crystalline or glassy, appears to be about 1.62 Å. The numbers under the peak are the average number of atoms surrounding each silicon; the fact that all the numbers are above 4 is probably without significance and to be ascribed to the error of the method.

Since in the soda-silica glasses the number of oxygen atoms is greater than twice the number of silicons, part of the oxygens must be bonded between two silicons, as in silica glass, and part to only one silicon. The next two peaks on the curves for the soda-silica glasses correspond to the sodium-oxygen and the oxygen-oxygen distances, and the numbers under the peaks at 2.35 Å are the calculated number of oxygens surrounding each sodium, which average about 6, within the accumulated experimental error.

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[54] Warren, B. E., and Loring, A. D., *J. Am. Ceram. Soc.*, **18**, 269 (1935).

[55] Warren, B. E., and Biscoe, J., *J. Am. Ceram. Soc.*, **21**, [7] 259-65 (1938).

The next larger distance of separation is that of two silicons bonded through an oxygen, which is 3.2 Å when the two silicons are diametrically opposite. This peak is evident in SiO_2 glass, but with higher Na_2O-content it becomes masked by a variety of other interatomic distances.

The curves of Fig. XX. 3 show that soda-silica glass is not a mixture of Na_2O and SiO_2 molecules, and that neither sodium metasilicate nor sodium disilicate molecules can exist. They do not make possible a discrimination between the hypothesis of a random network as opposed to a mixture of crystallites, but calculation shows the necessary dimensions of such crystallites to be about those of a single unit cell. "Since the essential feature in a crystalline network is regular repetition, the term crystalline ceases to have any meaning when applied to volumes of the order of one unit cell."

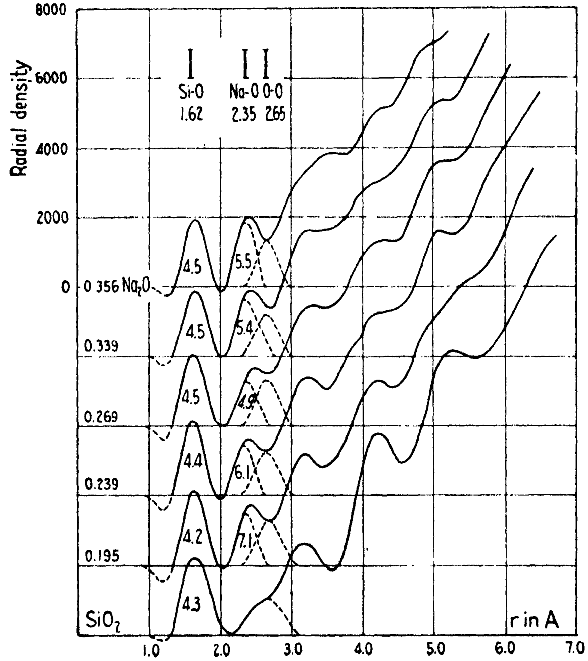

FIGURE XX. 3.—Radial Distribution Curves for Soda-Silica Glasses. After Warren and Biscoe.

"The x-ray results do not exclude the existence of a few small crystals in glass. Here and there, as part of a continuous variety of structures, a particular kind of structure might develop far enough to be called a crystal. The essential point is that true glass is a form of matter which has cooled too rapidly from the melt to allow enough systematic organization of the atoms to produce any appreciable amount of material which may be called crystalline." Certain haphazard configurations more or less closely approximating a crystalline configuration may be frozen-in.

The structure of soda-silica glass as deduced by Warren is shown in Fig. XX. 4. "Since the real structure exists in two dimensions, it is necessary to take certain liberties in making a schematic two-dimensional representation. In three dimensions each silicon is tetrahedrally surrounded by four oxygens, and in the two-dimensional representation each silicon is shown surrounded by only three oxygens. The oxygens are correctly represented, some of them bonded between two silicons, and others bonded to only one silicon. The sodium ions Na⁺ are shown in various holes in the irregular silicon-oxygen network. This figure repre-

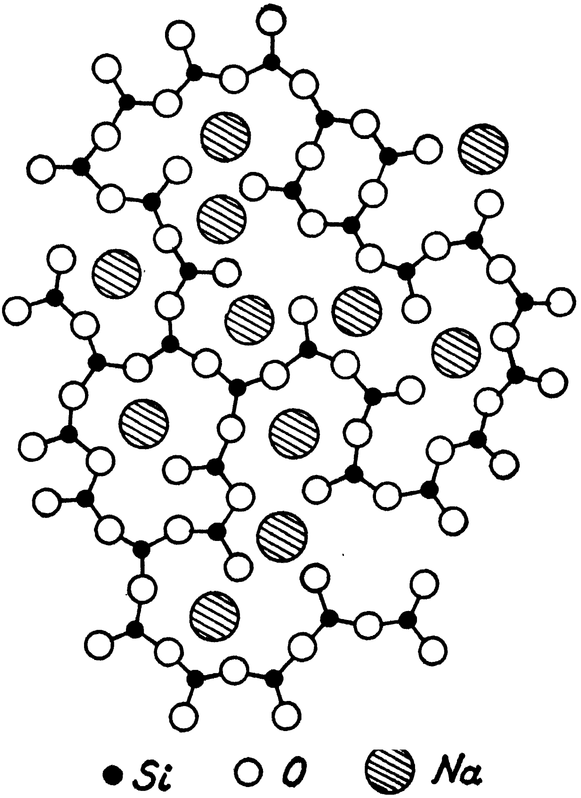

FIGURE XX. 4.—Schematic Representation in Two Dimensions of the Structure of Soda-Silica Glass. After Warren and Biscoe.

sents very well the essential scheme of structure in a soda-silica glass. There is a definite scheme of coördination; each silicon tetrahedrally surrounded by four oxygens, and part of the oxygens bonded between two silicons and part to only one silicon. The sodium ions are held rather loosely in the various holes in the silicon-oxygen network, and surrounded on the average by about 6 oxygens. Although it is a perfectly definite scheme of structure, there is no regular repetition in the pattern, and hence the structure is non-crystalline."

There is no regular repetition, and soda-silica glass has no definite chemical composition. As the soda content is increased and the proportion of oxygen atoms to silicon atoms increases, more and more of the oxygens are bonded to only one silicon, and more and more sodium atoms find places in the irregular openings in the three-dimensional silicon-oxygen network. The atoms of that network oscillate about average positions as the result of temperature motion, and under the influence of an electric field the sodium ions readily migrate from one hole to another, and the electrical conductivity is due to this stepwise migration.

The lowering of the softening point of silica glass on addition of soda is the result of breaks in the silicon-oxygen framework resulting from an increasing number of oxygens being bonded to only one silicon, and as more and more of these bonds are broken the structure becomes less rigidly braced in three dimensions. "Since there is no scheme of repetition in the glass, no two points are exactly identical. There are points with widely varying degrees of weakness, at which flow or breakage can occur at a continuous variety of temperatures. Hence it is readily understood why glass gradually softens, rather than having a definite melting point like a crystal."

The picture of the structure of glass worked out on the basis of x-ray studies by Warren, which is in agreement with the theoretical deductions of Zachariasen, is one of a random non-repeating and non-symmetrical network. It is in complete agreement with the concept of the constitution of glass as that of a typical liquid, in which the atomic configurations characteristic of some high temperature have become fixed by reason of the great viscosity of glass at ordinary temperatures. It is in accord with the definition: A glass is an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of that substance, but which, as the result of having been cooled from a fused condition, has attained so high a degree of viscosity as to be for all practical purposes rigid.

Index

This Index lists only the initial page of the discussion of a particular subject when the discussion extends without a break over several pages; but whenever a paragraph dealing with another subject intervenes, a new entry appears. The references to an author are grouped, whenever possible, according to his several publications, each of which is indicated in the Index by the year date of the publication in parentheses preceding the page references to it. A reference solely to a Table or a Figure on a particular page is indicated by the letter "T" or "F" following the page number; but if the reference is also to the text on the same page, the "T" or "F" is in parentheses. Tables and Figures have not been indexed under the names of authors except in those few cases in which separate literature references are appended to a Table.

Chapter headings are marked by inclusive pagination in bold face; the most important of several page references under a subject entry is marked by a single number in bold face. The word "glass" has been omitted from most headings in the Index, as, for example, "dielectric constant (of glass)." A heading containing "effect," "point," "temperature," etc., preceded by an adjective is listed only under the adjective, as "Kerr effect," "melting point," and "liquidus temperature."

The properties of a substance have been listed under the name of the substance; but the names of substances have not been listed under a property. Individual compounds and glasses having specific names are listed in the main index; but glasses containing two or more components are listed separately at the end. The systems are arranged there in accordance with the periodic table. To avoid duplication of entries under related properties, a number of them have been combined under one heading in several instances, as shown in the following list which applies only to the lists of properties as subheadings and not to the primary headings:

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annealing point		annealing characteristics
annealing range		annealing characteristics
annealing temperature		annealing characteristics
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birefringence		optical properties
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compressibility		elastic properties
critical temperature		annealing characteristics

crushing strength		strength
cubic expansion, coefficient of		expansion
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dielectric strength		dielectric properties
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