SILICATE SCIENCE

BY

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VOLUME VIII

INDUSTRIAL GLASS: GLAZES AND ENAMELS

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To the Memory of

KAMILLO KONOPICKY

Preface to Volumes VII and VIII

In general, Volumes VII and VIII are organized in the same manner as Volume II, Sections A and B. The numbering system used for paragraphs facilitates cross-referencing and index entries.

Advances made in silicate research from 1960 through 1970 are presented. Although much of the discussion is still based on the classic physical chemistry theories, an attempt has been made to introduce the essential solid state physics principles and to show how they can be applied to noncrystalline solids. The properties of many diverse vitreous materials are presented.

All of the international literature was examined in its original form by the author. Some came from the author's own collection of periodicals and books and some from The University of Toledo, the Toledo-Lucas County Public Libraries, and from the Library of the State of Ohio. The kind cooperation and help of the National Library Loan Service in obtaining rare literature are greatly appreciated.

When original texts were not available from any source, abstracts were used which, though critically chosen, sometimes lacked the information sought. Selected abstracts, however, have been included, but only when they could function as a guide to the reader's special endeavors.

These volumes complete this treatise. It is hoped that the information they supply will lead to fruitful research in the future.

The author is deeply grateful to Dr. W. C. Carlson, the previous President of The University of Toledo, to his successor Dr. G. R. Driscoll, and particularly to Dr. J. R. Long, previous Executive Vice President, and to his successor Dr. Robert S. Sullivant for their kind understanding and advancement of this enterprise during which the author enjoyed liberal hospitality as Professor Emeritus. The facilities of the Villa House of Cheltenham were placed at his disposal. The Board of Trustees of this University is sincerely thanked for providing financial aid for clerical help and for the administration of the Institute of Silicate Research.

Special gratitude is due Mr. P. T. Barkey, Director of the University Libraries, and his staff, especially to Mrs. I. J. Weis and to Mr. J. M. Morgan, for their help in supplying bibliographical material not only from the local libraries but from many

outside organizations. A debt of thanks goes to Mrs. B. M. Lorenzen and to Mrs. J. H. Kent, the author's personal secretaries, and to Mrs. B. G. Kirkpatrick who helped so much in preparing the many manuscripts and in keeping organized the tremendous amount of material to be examined through the many stages of proof. The accurate secretarial assistance of Mrs. M. Foster and Mrs. J. S. Barnes is greatly appreciated.

A good deal of energy was expended in securing and selecting the best available original illustrations for these volumes. We received invaluable aid from competent laboratories and special departments of The University of Toledo in reproducing, enlarging, and correcting the illustrations used, particularly from the staff of the University's Office Manager in Education, Mr. W. Douglas, and the Print Shop Manager, Mr. J. L. Clemens.

Our sincere thanks go to the numerous publishing organizations and editors who helped our enterprise by granting the necessary permissions to reproduce illustrations from their original literature.

Finally, it is the author's privilege and pleasure to express his deepest appreciation to Mr. Frederick K. McIlvaine for his editorial assistance in the form of valuable advice and discussions on the manuscripts for these volumes, essentially contributing to their readability.

Wilhelm Eitel

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*General Introduction**

1. The present state of the art of glass manufacturing, or glass technology in the meaning proper for this text, is based on the developments of glass melting units over several centuries, from the primitive forms of pot furnaces of little capacity to modern tank furnaces that make possible the production of several hundred tons of glass a day. These furnaces are so well and richly described in the technological literature that we feel obliged to only make brief reference in this volume to the many possibilities for improvement and modification of the traditional forms and constructions beyond tank furnace to units equipped for glass fusion. These will not advance any essentially new principles beyond the classical reactions and operation for glass fusion from a "batch" consisting of the fundamental mixtures of mineral raw materials like quartz (sand), limestone, or dolomite, in combination with such chemicals as Na_2CO_3 or Na_2SO_4 as the simplest ingredients. Progress actually made in the last decades did not concern the basic concepts of the production from the batch in tank furnaces as the given tool of the industrial processes, but came in improvement of the heat economy of the furnace system, and acceleration of treatment of the batch to achieve homogenization and fining. These evolutions of the last decade will therefore be the subject of our introductory chapter.

2. A few remarks may be appropriate concerning the great and promising prospects offered by modern electric engineering through special modification of the usual glass fusion methods to gain essential advantages in the thermochemical balance aspects of corresponding new construction of electrical glass furnace. Such units create new possibilities for the manufacturing of special glasses which, because of their contents of highly corrosive or highly refractory batch components cannot be melted in the classical tank or pot furnaces. They require walls and linings of refractory ceramic materials which are much different and, in principle, new con-

*All volumes of "Silicate Science" have been published by Academic Press, New York. Vol. I, 1964; Vol. II, 1965; Vol. III, 1965; Vol. IV, 1966; Vol. V, 1966; Vol. VI, 1975; Vol. VII, 1976. Where a reference is listed by volume and paragraph number, this treatise is indicated.

tainer materials (refractories) such as noble metals of the Pt group, Wo, Mo metal, and the like. When high electrical current intensities must be applied in such cases, the fusion may be achieved in modern electric arc furnaces. Abundant literature on this process is available from the experience of electrometallurgy.

3. We will omit discussions of this wide and extremely specialized field of glass engineering, referring, however, to such excellent and comprehensive reviews as we have at hand. These include a publication by E. Plumat, P. Éloy, J. Duthoit, and J. Cl. Barbier† which not only outlines possibilities for evolution in glass fusion furnace construction, but also offers details for improvement of the efficiency of the different systems concerned. Later in this section we will call attention to important improvements in reactions of the batches, the homogenization and fining of the raw melts, and the behavior of the glass melts when refractories come into contact with the molten material. Plumat *et al.* give so many instructive examples for improvement to be proposed and others performed in the last 10 years that we feel justified in restricting consideration here to the physical and chemical reaction phenomena which normally occur in every glass tank furnace, and in electric furnaces of many shapes. This will be a rich source of information and recommendations for advancement. Studies of the more than one hundred references presented in Plumat's review are an excellent and adequate introduction of the student to patent literature on glass fusion units.

†*Glastech. Ber.* **40**, (11), 411–425 (1967).

Chapter I

Part A: Reactions of Glass Batch Mixtures at Elevated Temperatures

INTRODUCTION

4. As an instructive introduction to the physical–chemical basic reactions in batches for glass compositions of the common Na–Ca type we recommend the interesting report by K. Kautz and G. S. Stromburg[1] which starts from results essentially disclosed in reports by G. Tammann and W. Oelsen (1930), O. Knapp (1934), C. Kröger and J. Blömer (1958), and more recently by F. W. Wilburn, S. A. Metcalfe, and R. S. Warburton.[2] Most of these investigations were made by determination of reaction rates in the batches, measuring the temperature ranges for the appearance of definite phases which are different from those in the original batches, and are characteristic of partial reactions of the mixes. Kautz and Stromburg paid special attention to the changes in the raw materials, namely, quartz (sand), $CaCO_3$ (present as limestone, or in dolomite), and alkalies in the form of commercially pure Na_2SO_4. The nature of the new-formed compounds was examined by the classical methods of polarization microscopy techniques.

5. The application of a special gradient furnace[3] with an accurately controlled rate of heating and gas atmosphere is paradigmatic. The observed results were supplemented by the microscopic evaluation of thin sections and X-ray diffraction analysis of the crystalline phases. For the control of the water content in the batches and reaction products, infrared absorption spectroscopy proved to be an important help. Beside the α-III modification of Na_2SiO_3, CaO, and Na–Ca-double carbonate, the crystallization of $Na_4CaSi_3O_9$ was established, whereas $Na_2Ca_2Si_3O_9$, as de-

[1] *Glastech. Ber.* **42**, (8), 309–317 (1969); see also the comprehensive literature references presented by K. Kautz, *ibid.*, (6), 244–250.

[2] *Glass Technol.* **6**, (4), 107–114 (1965); see ¶ 16.

[3] Cf. K. Beyersdorfer and J. Hammer, *Ber. Deut. Keram. Ges.* **42**, (2), 44–49 (1965).

scribed by Kröger and Blömer was uncertain. From the glass technological viewpoint, it is significant that definite variations in the presence of the crystalline phases after the batch reactions were observed as a function of variable grain sizes on the reagents, the batch composition, and their moisture contents. There were characteristic differences between the products of the laboratory experiments and samples taken from industrial batches in the furnace process although, in most cases, the samples had been treated equally in the gradient temperature process. The experiments of Kautz and Stromburg, on the other hand, definitely confirm Kröger's conclusions on the importance of the presence of moisture in the furnace atmosphere and of "impregnation" effects; the existence of the latter was confirmed anew.

6. The *moisture content of glass sand* as an essential constituent of glass batch mixes, plays a very important role eventually as an accelerating agent for the fusion of the batch, and the fining of the glass melt. Its accurate determination and the constant survey for its presence are therefore some of the most important problems in glass manufacturing.[4] For all these reasons it is indispensable to organize periodically a regular and accurate survey of the moisture in commercial glass sands before they are introduced to batch feeding operation for which the nuclear methods using rapid neutrons in their interreaction with hydrogen cores (protons) are particularly attractive.[5]

A recent publication by V. Caimann[6] refers to more developed instrumentation for the current automatic survey of moisture determinations and digital-counter statistical evaluation for the plant control of glass sands, using a 100 (or better 300) Ci $-{}^{241}$Am $-$ Be source and an impulse-time counter (scintillometer) system. The accuracy for single measurements could thus be reproduced to ± 0.1 wt. % H_2O.

7. In order, as far as it is possible by simple technological measures, to reduce uncontrolled divergencies in the course of batch reactions in the early stages of their evolution in the tank furnace atmosphere, *granulation*, or *pelletizing*, of the batch mixtures by compacting treatments were again and again proposed, going back to recommendations of G. Keppeler (1929) and J. Löffler (1951). They now have been emphasized by S. Kirchhof[7] who constructed a rotating granulation panel which was adjustable to an optimum axial inclination of the pan, normally for an angle of 35° to 55° to have a reproducible efficiency comparable to that of the well-known

[4] Cf. the classical studies of batch reactions in many papers by C. Kröger *et al.*, *Glastech. Ber.* **29**, 275–289 (1956); **30**, 42–52 (1957); but also older literature, e.g., of F. Zsckacke, *et al.*, 1938.

[5] See older literature by E. Amrhein, A. Dietzel, and K. Metzner, *Ber. Deut. Keram. Ges.* **37**, (7), 311–315 (1960); H. Neuhaus, G. Hombeck, and W. Kühn, *Arch. Eisenhüttenw.* **82**, 1017–1026 (1962).

[6] *Glastech. Ber.* **45**, (6), 247–256 (1972).

[7] *Silikattechnik* **13**, (9), 325–329 (1962).

granulator pan of the Lepol process in the production of granules for Portland cement production from raw mixes. Kirchhof is of the opinion that granulation of such a type is superior to mere compaction of the batch mixtures in briqueting or pelletizing.

8. J. Yamamoto and E. Komatsu[8] studied the same problems emphasizing that the batch granules contribute very much to the desirable rapid reactivity of the constituents in the early fusion processes because of the conspicuously improved heat conductivity of the granules. Both authors recommended addition to the raw mixed batch of binders consisting of NaOH brine mixed with 50% soda in order to reach a satisfactory mechanical rigidity of the granules. Industrial experiments on a large scale produced high rates of fusion and higher outputs of glass when granules, and not the common charging practice, are used. It must, however, be emphasized that the fining must be carefully controlled with batch granule charges. Practically the same favorable results were presented by M. A. Matveev and B. K. Demidovich,[9] particularly by adding alkali to the batch to increase plasticity, and thus gain better rigidity and mechanical stability of the granules.

9. An extensive comparison of briqueting with granulation practice in preparing glass batches was presented by O. Knapp[10] in a special report on more than 10 years practical experience in a Hungarian glass plant. As a plastifier for the batch mixes, Knapp used, for briqueting, ammonium sulfate, slaked lime, water glass, starch, Portland cement powder, or Na silicofluoride. The granulation process has definitely a better energy economy. A report presented by H. J. Illig[11] emphasizes the absence of troublesome dusting of the batch when granulation is used for the compaction. Recommendations are made for optimum ratios of the solid to liquid phases in the granules and the conditions of the panel rotation, the drying of the products, and the behavior after drying and the final stability. Rapid escape of the reaction gases from the granule structure in the early stage of fusion is important. The granules must not be too hard, to avoid explosive dusting and material losses, which cause corrosion of the refractories of the regenerative system of the furnace and other troubles.

ELEMENTARY BATCH REACTIONS

10. The melting down process of normal batches was extensively observed by high-temperature microscopy by H. Jebsen-Marwedel and W. Buss.[12] Their most

[8] *Glass Ind.* **49**, (9), 491–493 (1968).
[9] *Steklo Keram.* **24**, (9/10), 561–564 (1967).
[10] *Glas Email Keramo Tech.* **20**, (5), 166–169 (1969).
[11] *Silikattechnik* **22**, (1), 7–12 (1971).
[12] *Sprechsaal* **95**, (9), 199–212 (1962).

instructive series of micrographs show many details of the fusion as such, and demonstrate the importance of the grain-size gradation of the reactants. Specifically, the behavior of the Na sulfate in the progressive homogenization of the glass is most evident. The sulfate is of great efficiency for avoiding troublesome conglomeration in the batches, and for a normal digestion of larger lumps, by considerably improving surface wetting of lime and dolomite particles. The latter additive is particularly critical because it has a relatively very slow reaction with the primary melt phases, often retarded up to 1300°C. Sources of local heterogeneities in the reacting batches may sometimes stubbornly subsist, thus retarding the fining (see later) at temperatures up to 1400°C (for common window-glass-type glass melts).

11. Advanced *interference-microscopic methods* for studying glass batch reactions and the diffusion in them were developed by J. Löffler,[13] chiefly for the examination of the later stages of batch reactions in glass fusion and the problems of reaction residues. Löffler's observations excellently illustrate the diffusion processes in action around residual quartz grains in the not yet fully homogenized glass material. The "digestion" of residual single sand grains was observed in detail. These experiments made evident that the digestion is not only a dissolution process of the quartz phase, but that it is combined with the more or less rapid inversion of quartz into tridymite and cristobalite under the influence of an alkali-enriched primary glass melt originating from the liquefaction of the batch. This phase gives a particularly increased, surface-active, spreading tendency on the phase boundaries, and all premises are locally fulfilled for an application of Jebsen-Marwedel's theory of "dynacticity" (cf. ¶ 174, 182, 185 ff.).[14] The alkalies migrate from the surrounding of the sand residual grain onto the glass surface, and a silica-enriched melt zone develops which helps to accelerate the homogenization process. The rates of such reactions may considerably vary from grain to grain, and also the possibility of a typical conversion "aureole," namely of *cristobalite* formation, was observed (cf. Fig. 1) which is finally dissolved.

12. Another very instructive method for the experimental observation and measurement of the dissolution kinetics of quartz in batches and melt phases was described by K. G. Kreider and A. R. Cooper,[15] characterized by the use of *spherical* quartz crystals (of 2.00 to 2.84 mm in diameter) as the samples which were exposed to molten Na silicate (with 40 wt.% Na_2O) at a constant temperature of 950°C. The molecular diffusion coefficient was 4.4×10^{-6} cm²/second. In such systems a certain unexpected divergency in the dissolution rates of larger and smaller spheres was

[13] *Glastech. Ber.* **36**, (9), 356–370 (1963); **36**, (11), 453 (1963).
[14] Cf. *Glastech. Ber.* **29**, (6), 233–238 (1956).
[15] *Glass Technol.* **8**, (3), 71–73 (1967); an important correction in *ibid.* **9**, (1), 21 (1968).

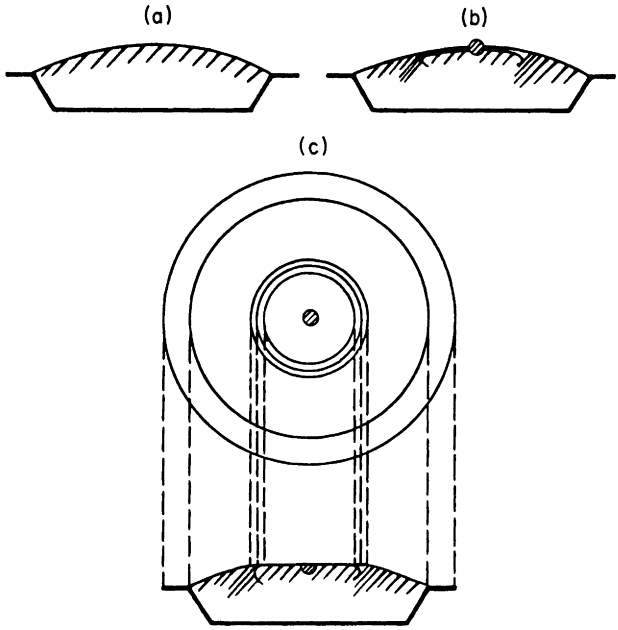


FIG. 1. Evolution of a spreading aureole around a sand grain in center, in vertical sections and horizontal projection (Löffler.) (a) shows the glass with a surface skin, impoverished in alkali; (b) the sand grain in the center of the surface layer from which silica-enriched glass spreads away, simultaneously somewhat shoved together; (c) the same, as seen projected from above.

observed. The latter spheres were more slowly dissolved (cf. ¶ 69). An interpretation of this fact is possible from density convection effects which, however, can be eliminated by an elementary extrapolation of the results for the sphere radius = 0, in the calculation of the diffusion coefficient. Interesting is a curve presented for the (dimensionless) time required to reach half-size as a function of the original radius at 950°C.

13. In principle, the same method was applied to reach half-size by J. Hlaváč and H. Nademlýnská[16] for the dissolution of quartz and silica glass spheres in a melt of Na disilicate under the conditions of molecular diffusion (cf. Figs. 2a,b). The results could be evaluated for the coordinates t/a_0^2 and $t^* = Dt/a_0^2$ in the theory of the molecular diffusion coefficient. The effective diffusion coefficients are in the order of magnitude of 10^{-7} to 10^{-8} cm²/second, the activation energy = 34 kcal/mole for temperatures between 900° and 1200°C. The differences in the rate of activation for quartz and silica glass are inconsiderable, although there is a distinctly larger

[16] *Glass Technol.* **10**, (2), 54–58 (1969).

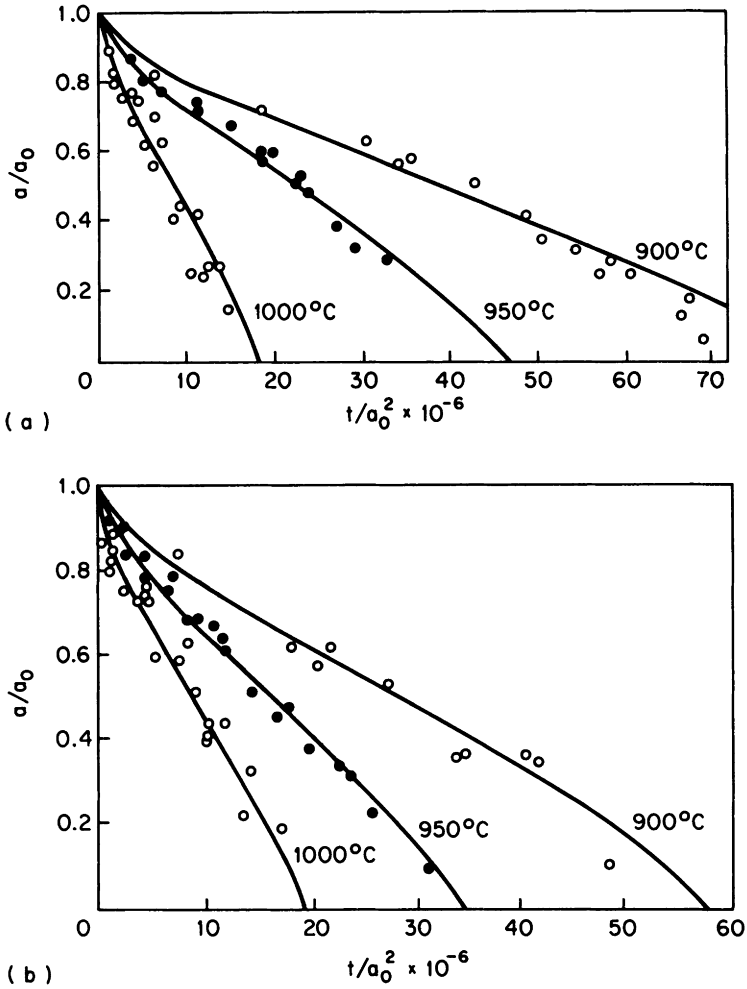


FIG. 2. Dissolution of quartz (a) and vitreous silica spheres in sodium disilicate melt (b) at 900°, 950°, and 1000°C; diffusion coefficients $D \times 10^8 = 1.8$, 2.8, and 6.4 for quartz (a), and 2.1, 3.1, and 5.1, for silica glass (b). (Hlaváč and Nademlýnská.)

scattering and a deviation from a strictly straight linear functional relation between t/a_0^2 (experimental), and Dt/a_0^2 (theoretical).[17]

14. How polycrystalline cristobalite, shaped in cylindrical *rods* (diameter 2 mm) behaves in low alkaline borosilicate glass melts (concentration of R_2O between 0

[17] On the theory of the molecular diffusion see D. W. Ready and A. R. Cooper, *Chem. Eng. Sci.* **21**, (10), 917–920 (1960).

and 10 wt. %, ratio Si/B = 1.74) was demonstrated from a more practical viewpoint by E. F. Riebling[18] (cf. Vol. VII, ¶ 437) above 1300°C. The result was a satisfactory prediction of the time for the complete dissolution as a function of temperature, ±10% as the limits of accuracy. Riebling emphasized that the inversion of quartz into cristobalite in the original material exposed to melt corrosion above 1250°C is a normal phenomenon. The practical meaning of these interesting experiments consists particularly in the consideration of the conditions for glass fusion on an industrial scale, involving convective flow phenomena. Riebling proposed complete dissolution curves for cylindrical, spherical, and tabular samples and for the condition $c/c_0 = 0.3$ (namely, the ratio of interface concentration of the diffusion species, the concentration on the sample surface) and the extent of dissolution as a function of Dt/R^2 (cf. Fig. 3).[19]

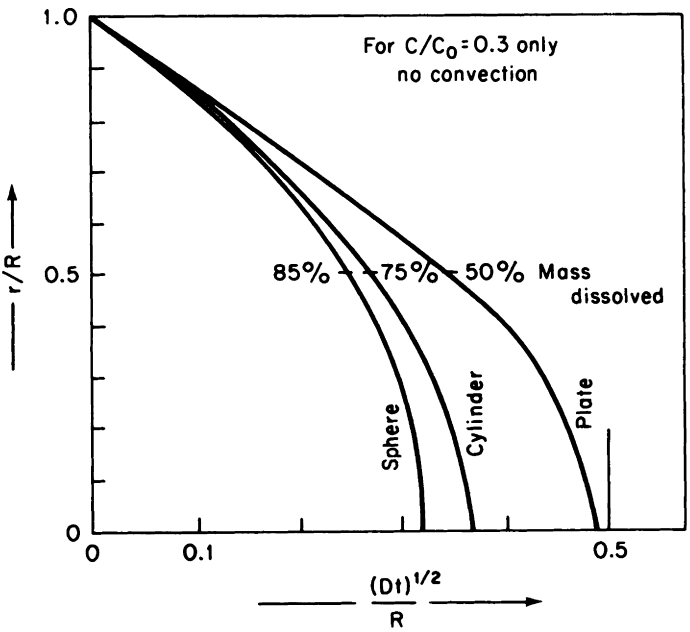


FIG. 3. Proposed complete dissolution curves for glass cylinders, spheres, and plates. (Riebling.)

[18] *Amer. Ceram. Soc. Bull.* **48**, (8), 766–769 (1969).

[19] In the theory of diffusion after J. Crank, cf. "Mathematics of Diffusion," by Oxford Univ. Press, London, 1956, pp. 46, 62, 67, 86; and Kl. Schwerdtfeger, *J. Phys. Chem.* **70**, (7), 2131–2137 (1966); see also R. Heimann, *Glastech. Ber.* **43**, (3), 83–88 (1970); with valuable literature references; R. Heimann, Ph.D. dissertation, Free Univ., Berlin, 1966, on the dissolution of quartz spheres in molten NaF.

15. R. Heimann and A. Willgallis[20] emphasize that not only chemical corrosion but also internal stresses in quartz when suspended in melts (these may be alkali silicates, borates, phosphates, fluorides, or the primary melts in the batch fusion process) must play an important role in the fracturing caused by the progressive inversion of quartz to tridymite and cristobalite. This is connected with considerable volume increase effects caused by the phase transitions[21] as shown in the instructive Fig. 4. Heimann and Willgallis describe experiments with quartz grains exposed at 1100°C in melts of $Na_2Si_2O_5$, Na_2SiO_3, and alkali tetraborates as observed in the Leitz microscope stage furnace. The early stages of cracking can easily be made visible by staining with dibromo-*o*-cresol sulfonophthalene which is highly sensitive method for the detection of textural discontinuities, and indicates polymorphic inversion effects of tridymite and cristobalite at 180° and 270°C.

HETEROGENEITIES IN PRIMARY BATCH REACTION PRODUCTS

16. In continuation of previous studies, M. Jaupain and D. Brichard,[22] A. Dietzel, O. W. Flörke, and H. Williams[23] demonstrated how partial melts may flow out from the full batch of an industrial furnace and produce a characteristic differentiation from sand particles and coarser granular fragments of limestone and/or dolomite. Volatilization of alkalies and B_2O_3 may contribute to heterogeneities in the batch pile which in later stages are observed in the form of dissolution striae and cords (cf. ¶ 183 ff., 484, 488 ff.). A particularly strong differentiation occurs when the batch is molten in fireclay crucibles ("pots"), whereas feldspar is a good flux which is rapidly assimilated. In many respects the picture of the fusion process is different when the batch does not come directly into contact with the fireclay walls but when it is molten above a layer of prefused glass. CaO-enriched striae with loosened residual residues of limestone particles will sink through the glass layer and spread under it to the pot bottom, without homogenization. Crystallization of $Na_2O \cdot 2CaO \cdot 3SiO_2$ in this product indicates this particular anomaly in the reaction sequence. A true gravitative differentiation takes place, in contrast to which the upper layers of the batch will be enriched in silica. The higher surface tension of the CaO-enriched bottom layer in comparison with the upper portions is, in addition, a factor of great significance in this segregation process. More harmful even are the highly viscous and only slowly assimilated striae formed when Al_2O_3 from fireclay

[20] *Glastech. Ber.* **43**, (1), 12–15 (1970).
[21] Cf. B. H. Bogardus and R. Roy. *J. Amer. Ceram. Soc.* **38**, (12), 573–576 (1963).
[22] Sympos. Fusion Verre, Charleroi, 1958, pp. 269–296.
[23] *Glastech. Ber.* **28**, (8), 322–329 (1965).

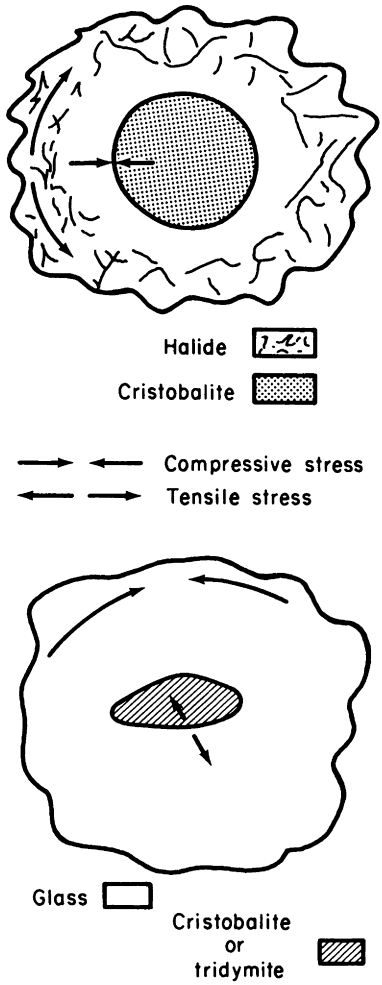


FIG. 4. Schematic diagram, showing sign of stresses in both systems with development of fractures in low-strength halides. (Bogardus and Roy.)

material interferes with batch reactions. Only an intensive mechanical stirring can accelerate the assimilation and homogenization in pot melts.

17. F. W. Wilburn, S. A. Metcalfe, and R. S. Warburton[24] presented impressive evidence of the high value of differential-thermal and differential-thermogravimetric analysis methods, in combination with high-temperature microscopic examination in studies of batch reactions, as demonstrated for the process of window glass manu-

[24] *Glass Technol.* **6**, (4), 107–114 (1965).

facturing on an industrial scale. It was possible in this way to draft a complete schematic succession of all the reaction details in tank furnace operation from the earliest reactions starting at 500°C with the formation of the double carbonate $Na_2CO_3 \cdot CaCO_3$, to the important temperature of 780°C which corresponds to its eutectic melt with $CaCO_3$, then to the temperature of beginning reaction of the carbonates with sand (quartz) at 850°C. This latter process is rather slow and takes place in the melting chamber of the tank furnace with a steadily improving homogenization, but even at 1100°C only about 86% of the sand is actually dissolved, i.e., residual sand grains may reach the fining zone of the furnace, when the flow rate of the glass melt is rapid enough. This also illustrates the tremendous importance of studies on the material flow and distribution over all the length of the tank, in combination with the temperature distribution from point to point (see ¶ 4). The many excellent and instructive diagrams presented by Wilburn *et al.* teach the basic importance of a carefully controlled regime of batch operation for reaching a satisfactory homogenization, fining, and a normal production. J. Robredo[25] came to the conclusion from analogous observations in practice that the application of differential-thermal analysis in batch control is a reliable and rapid method in all details of tank furnace operation, with the emphasis on the problems of homogenization.

18. The dissolution of residual quartz sand particles in the batch glass, before it enters the fining zone was specifically studied by M. Truhlářová and O. Vepřek[26] under the conditions of free convection. Silica glass rods dipping into a melt of Na silicate, or of Na – Ca silicate glass at 1200°C were rapidly inverted on the free surfaces to cristobalite from which the molecular diffusion and dissolution started in the same general aspects as we discussed above.

19. The use of NaOH in the place of Na_2CO_3 is an interesting variation of the principle of pretreatments of granulated batches or pelletized glass before the introduction into the fusion chamber of the industrial tank furnace, or at least of a partial pretreatment of the water-soluble chemical additives of the batch for a certain stabilization of the granules. Prereaction of NaOH with quartz sand facilitates the reactivity of the batch with limestone, dolomite, and other constituents considerably and contributes much for a homogenization throughout the raw glass melt. The chemical industry of organoplast manufacturing (in the process of Cl_2 preparation as an essential reagent in the polymer process) offers as a side product a brine with a content of 50% NaOH (if required also of 70%). This brine can be reacted in its mixture with quartz sand after shaping to granules, pellets, tablets, and the like to

[25] *Verres Refract.* **21**, (6), 539–549 (1967).
[26] *Glastech. Ber.* **40**, (7), 257–260 (1967); **42**, (1), 9–11 (1969).

sodium silicates by heating to a minimum temperature of 320°C and calcined to an easily manuable raw material at 800°C in a separate reactor, or in fluid-bed processes with hot air, directly added then to the other batch ingredients and reacted in the glass fusion chamber of the tank furnace.[27] The process is described in detail by A. Delcoigne and R. Matmuller,[28] with calculations of the heat economy and thermal balance data, which demonstrate the promising aspects for a future practical verification of the method.

20. The reaction kinetics of batches consisting of simple mixtures of quartz and the carbonates of Li and Cs were investigated by M. A. Matveev and B. N. Frenkel[29] for different ratios R_2O/SiO_2 (from 1:1 to 1:5) and over the temperature range from 530° to 910°C for the system with Cs_2O and from 30.3 to 38.1 mole % Li_2CO_3, at 600° to 935°C, respectively. The grain size of the quartz (rock crystal quality) was variable between 0.064 and 0.072 mm; the rate of reactions strongly depended on this size. The gravimetrically determined losses in CO_2 were the basis for the calculations; the activation energies for the reactions were determined above and below the fusion points of the carbonates. In the place of the classical W. Jander equation, its modification by A. M. Ginstling and V. I. Brounshteĭn was used in the calculations of the rate constants. By X-ray diffraction analysis the meta- and disilicate phases could be confirmed in the reaction products; another, not accurately identified phase also appeared. Indications were observed for the occurrence of distinct unmixing heterogeneities in the products for the system Li_2O-SiO_2 (cf. Vol. V.A. ¶ 49 f., 54, 80).

21. The reactivity of quartz with melt solutions of basic alkali salts is of high importance because of the high fluidity in halogenide salt melts, not only in batches for glass manufacture, but also for the dressing of metal ores, the slag formation in metallurgical processes, and the slagging of refractories. For the surface-area evolution the rate of dissolution plays the decisive determining role; at high temperatures, however, the diffusion phenomena are predominant. A. Packter and F. W. Berk & Co. Ltd.[30] studied the reaction rates of quartz with MOH, M_2CO_3, and M_2SO_4, in melt solutions in LiCl and NaCl as the solvents, and with concentrations of 4–20 g ions/liter, at 450° to 600°C for LiCl, 1000°C for NaCl. When the weight losses are $\Delta\omega$, the relation $(\omega_t^{1/3} - \omega_t^{1/3}) = kt$ is valid for the three-dimensional, purely chemical diffusion rate determining the overall reaction

[27] Cf. G. Gringras, French Patent No. 1,469,109, Jan. 2, 1967.

[28] *Verres Réfract.* **25**, (6), 237–241 (1971).

[29] "Glass Forming Systems and Materials" (Yu. Ya. Eĭduk, ed.), pp. 9–16, 17–24, Izdat. Zinatne, Riga, 1967.

[30] *Silicates Ind.* **33**, 341–345 (1968).

kinetics.[31] Quartz reacts with NaOH at about 600°C by a purely diffusion-controlled rate constant. The reaction for the quartz surface is represented by diagrams showing it as a function of the anion concentration, C_{A^-}, and the activity, α_{A^-}. The rates of interaction decrease in the order $k_{(SiO_2-\mu OH)} > k_{(SiO_2-\mu_2CO_2)} > k_{(SiO_2-M_2SO_4)}$. LiOH shows extremely anomalous activities in LiCl solutions; the activation energies are for the Li salts 23 kcal/mole anion, for the Na salts 20 kcal/mole anion (cf. Vol. V.B. ¶ 117).

22. Even small amounts of distinctly fluxing agents may accelerate substantially the rate of melting down the batch mixes as was demonstrated by L. Šašek.[32] By differential-thermal analysis, thermal-gravimetric determinations, and measurements of the electric conductivity of the batches during heating, a complete description of the step-by-step changes in the melting processes could be developed. Starting from fluoride-activated reactions of soda with carbonate raw materials, it was established that the fluorides do not participate in the reactions as such; however, above 950°C NaF is volatilized from the batch mixtures, at the same time as an addition of NaF is made. An optimum of the melting down effects was reached (for a common Na–Ca silicate batch) when 0.64% and 0.266% SO_3 (introduced as Na_2SO_4) were added to the batch. Fluoride additions do not exert any undesirable crystallization tendency in the fresh-formed glass, but they are definitely favorable acting in fining processes.

23. H. Scholze and E. Galanulis[33] observed in the heating microscope the rate of dissolution and assimilation of limestone and dolomite in the primary batch melts for a Na–Ca silicate glass. Its viscosity increases somewhat in the early stages of the carbonate-sand reactions at low temperature, but later shows the inverse tendency with increasing temperature, and CaO is dissolved. At 1200°C the viscosity is rather high if the batch glass reaction immediately surrounds residual limestone grains, but with increasing temperature it lowers rapidly in agreement with the phenomenon of a rather sudden dissolution of the lime in the raw glass above 1200°C as can be observed in the batch fusion chamber of the tank furnace. The dissolution and final assimilation of dolomite grains comes to an end more rapidly than they do with limestone, evidently by a certain fluxing action effect of MgO in dolomitic limestones and related raw materials. As a measure of the rates of dissolution, one may use the product Dt, of the diffusion constant and time.

[31] Cf. L. Reed and L. R. Barrett, *Trans. Brit. Ceram. Soc.* **63**, (10), 509–534 (1964), who studied the slagging of refractories.

[32] *Collect. Paps. Chem. Technol. College, Prague, Sect. Inorgan. Chem. Technol.* B **9**, 201–228 (1966).

[33] *Tonind. Z.* **90**, (4), 145–146 (1966); in continuation of H. Jebsen-Marwedel's and W. Buss' experiments, *Sprechsaal* **95**, (9), 199–212 (1962); cf. ¶ 9.

24. It should be remembered that for the early reactivity in the soda- and limestone-containing glass batches one must, according to H. W. Billhardt[34] take into account polymorphic inversions of Na_2CO_3 at 350° and 480°C which are easily detected by X-ray diffraction analysis in a suitable high-temperature chamber, and particularly distinctly in an automatic self-recording Guinier camera (so-called nonius-camera). Also the double carbonate $Na_2CO_3 \cdot CaCO_3$ undergoes polymorphic inversions at 390° and 440°C which complicates the phase equilibrium diagram of the fundamental system $Na_2CO_3 - CaCO_3$, as was first studied by P. Niggli (1916) and is shown in Fig. 5. It is, nevertheless, remarkable that a compound $Na_2CO_3 \cdot 2CaCO_3$, which would be identical with the mineral *shortite*,[35] could not be detected by the X-ray diffraction (powder) method in the reaction mixtures.

25. M. I. Manusovich, V. V. Pollyak, and E. I. Smirnov[36] discussed the technologically important effects of variations in the composition of glass batches on the homogeneity and quality of industrial window glass. We are not able here to discuss the details in the basic furnace operation for an optimum which was achieved in the observations and calculations of the authors, but we may emphasize how important is an accurate familiarity with the physical-chemical conditions of the batch treatment in the modern glass production on a large scale. Even details of irregularities in the reaction and in the ensuing homogenization process of the glass are essential before it can leave the fusion chamber of the tank furnace into the fining section. As only one example of many we may emphasize how sand grains, before their complete dissolution, have the tendency to swim upward in the regular flow of the half-ripe glass, thus causing in the fusion zone local enrichments in silica and a characteristic formation of a so-called silica scum of low density, which is a most undesirable source for the evolution of siliceous striae (cords) in the final products. Relatively small changes in the composition and the thermal treatment of the batch may have great significance for a shifting of the scum lines and cause considerable deviations in the density and homogeneity of the glass and therefore trouble in working out. For all these factors the observations of Manusovich *et al.* are of great practical value as coming from a rich experience. They are illustrated by many instructive graphs and empirical equations.

26. American perlite (a volcanic natural rhyolite glass) as a raw material for industrial glass production was tested by M. G. Manvel'yan, S. R. Rustambekyan, and A. F. Melik-Akhnazaryan[37] specifically for the production in an electrically

[34] *Glastech. Ber.* **42**, (7), 272–276 (1969).
[35] Cf. H. I. I. Fahey, *Amer. Miner.* **29**, 514–518 (1939).
[36] *Steklo Keram.* **23**, (3/4), 115–118 (1966).
[37] *Steklo Keram.* **25**, (5/6), 294–295 (1968).

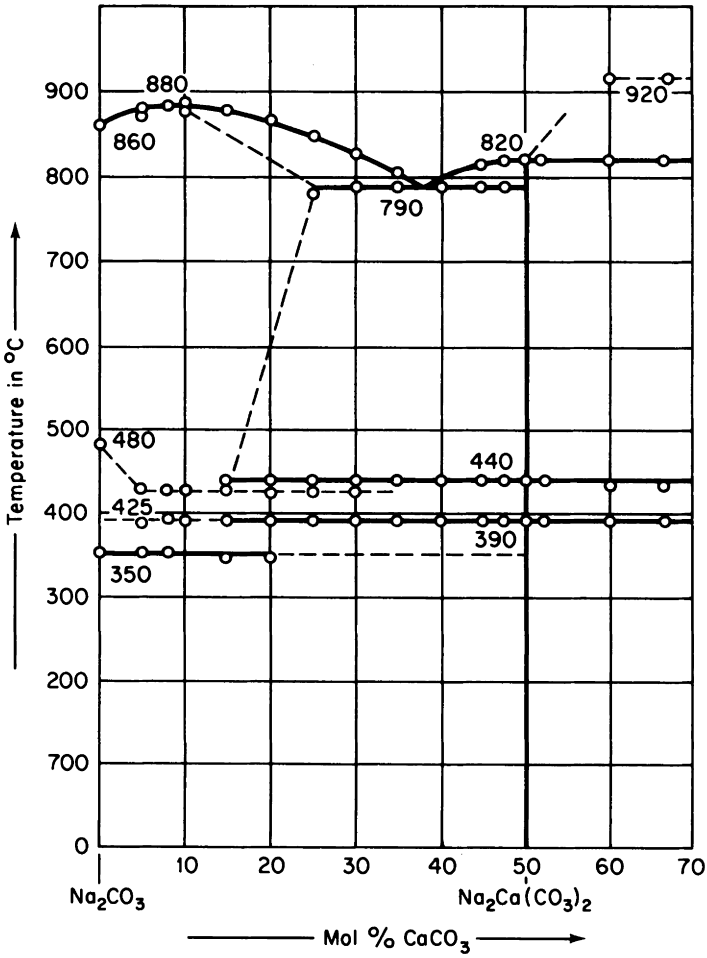


FIG. 5. Phase equilibrium diagram of system $Na_2CO_3-CaCO_3$ for p_{CO_2} = 1 atm. (Billhardt.)

heated tank furnace. An experiment to substitute the commonly used quartz sand entirely by such a perlite was not satisfactory because of an unexpectedly strong foam evolution. For this reason it was, nevertheless, observed that a partial substitution of sand by this natural, in the rock-analysis norm, feldspar-rich perlite glass material is very useful for the production of light-colored container glass of good chemical durability, relatively high in Al_2O_3, relatively low in alkalies and CaO, and containing staining oxides like FeO, Fe_2O_3, and Mn_2O_3.

27. The same may be said of the valuable observations of J. Klein[38] who used the Pauly-Erdey *derivatograph* (cf. Vol. III.A. ¶ 114, Footnote 160), Model OD 102, for a

[38] *Silikattechnik* **20**, (11), 372–379 (1969).

thorough study of the batch reactions with particular consideration of the heat transfer in the inner portions of the reaction mixtures at a conventional temperature of 800°C, and with increases of temperature up to 1430°C to observe the completeness of the vitrification process.[39] The derivatographic method disclosed particularly well the direct correlations existing between the indicated reaction effects (peaks on the recorded curves), with the silicate formation process, and the evolution of gases as decomposition products (Fig. 6). The final glass formation and homogenization no longer follow the laws of reaction kinetics; the rate of quartz dissolution is dependent on the rate of diffusion in the melt and the beneficial effects of *fluxing agents* like fluorides, sulfates, and KNO_3 (see above).

VACUUM MELTING OF GLASS; INFLUENCE OF THE FURNACE GAS ATMOSPHERE

28. For physical-chemical studies of the process of a vacuum treatment of normal glass batches, M. Boffé, G. Letocart, M. Pierre, and E. Plumat[40] described a

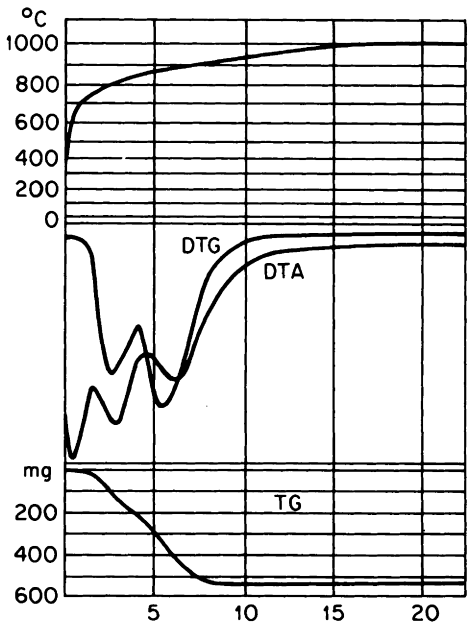


FIG. 6. Derivatogram for a typical industrial sand–lime–soda glass batch. (Klein.)

[39] See also previous experiments by A. G. Repa (1949–1955); and F. Ya. Kharitonov and L. G. Mel'nichenko, *Steklo Keram.* **20**, (7/8), 357–360 (1963).

[40] *Advan. Glass Technol., Tech. Pap. Int. Congr. Glass, 6th, 1962*, pp. 52–74.

fascinating series of systematically planned experiments made in a special furnace for reduced gas pressures in the primary atmosphere in the melting chamber. It is noteworthy that the effective reaction temperatures of the batches to fining could be considerably reduced, e.g., for a normal Na–Ca silicate glass batch to 1200° or 1300°C when the batch was prepared with NaOH as the essential alkali raw material, fine-ground quartz sand (grain size below 60 μ in diameter), CaO, and MgO. The accelerated optimum melts were very satisfactory in homogeneity, and well fined even when the fining period was relatively very short. Characteristic of the foam (scum) with very small bubbles on the free surface of the pot melts is its high content in H_2O, which is, however, rapidly reduced. Finally, the small bubbles are resorbed in the melt. It is technologically important that the number of bubbles remaining after the assimilation process and after restoring the normal atmospheric pressure greatly depends on the speed of this vacuum release. The longer this period, the lower the number of permanent bubbles.

29. C. Kröger and L. Sörström[41] measured the vapor pressure of silicate glasses and of their batch ingredients from the beginning of gas evolution of mixtures in the systems Na_2O-SiO_2, $PbO-SiO_2$, $Na_2O-B_2O_3$, and the corresponding systems including CaO. The most volatile oxides from such batches are Na_2O, K_2O and PbO. For the accurate measurement of the vapor pressures the Knudsen effusion method was used over temperature ranges from 800° to 1200°C and for pressures between 10^{-4} to 2.0 mm Hg; the vapors were condensed on Al foil covering a conical support, and weighted with a precision balance. It was rather irrelevant whether or not the Na–Ca silicate glasses were prepared from Na_2CO_3- or NaOH-containing mixtures since the resulting vapor pressure was practically the same. However, when Na_2SO_4 is present in the batch the measurements are not only much disturbed by the tendency of the melts to creep along the walls of the glass containers, but also by the adsorption of SO_3 from the furnace atmosphere onto the condensates. From borosilicate glasses the volatilization of RBO_2, as such, is noteworthy, whereas from PbO silicate glasses the dissociation of alkali plumbites to R_2O and PbO is very marked. The vapor pressure is in this case an exponential function of the SiO_2 concentration in the glass. The enthalpies and entropies of volatilization are approximately constant; only a slight minimum is observed for 90% PbO. With an increasing CaO content the Na–Ca silicate glasses show a maximum of vapor pressure on the isotherms at about 10% CaO, and similar phenomena for the specific electric conductivity.[42] Indications for the formation of Na-plumbite (see above) are observed for ternary Na–Pb silicate glasses of the *meta*-silicate composition type. In comparison with Na–Ca silicate glasses, the Na–Pb silicate glasses have vapor pressures which

[41] *Glastech. Ber.* **38**, (8), 313–322 (1965).

[42] Cf. H. Heckmann. Dissertation, Tech. Hochschule, Aachen, 1964.

are by two to three orders of magnitude higher than those of corresponding Na – Ca glasses, but the heats of evaporation are lower.

30. Corresponding measurements of vapor pressures of $Na_2SiO_3 \cdot nH_2O$ glasses (with $n = 2.6$ to 4.0) were made by H. Scholze and G. Gliemeroth[43] to which we here only briefly refer. M. A. Matveev and V. A. Krechmar[44] presented extensive investigations of the vapor pressures of glasses molten in an electrically heated vacuum furnace, e.g., a $Na_2O \cdot 3SiO_2$ model glass with measurements of equilibria pressures following an elementary empirical equation $\tau = a + bp$ for the time period τ of glass formation, in the temperature range from 1300° to 1000°C. For 150 to 300 mm Hg pressure the working conditions would be entirely adequate for an industrially promising glass production, with a rate of the homogenization period in the furnace, however, being 200 or 300% shorter than that of the analogous normal process.

31. Diffusion and solubility of CO_2, H_2O, O_2, N_2, SO_3, and other gases of technological significance in glass melts were studied by L. Němec,[45] as determined by vacuum extraction or a flushing process when the gases in the glass sample are replaced by inert foreign gases. Such measurements are generally made by the tensiometric method and thermal analysis, by chemical-analytical determination of combustion and decomposition products, measurements of partial pressures, and electrochemical methods, infrared spectroscopy, the determination of nuclear paramagnetic resonance, and last but not least, radioactive-tracer methods for systematically chosen indicator isotopes. The gases normally included in glass are either in a true solution state in the glass phase, or adsorbed, to be determined by their diffusion effects through a permeable (or semipermeable) membrane. A method specifically adapted for the resorption of the gases from gas bubbles may also be referred to here. It follows the principles indicated by Ch. H. Greene *et al.*[46]

Part B: Reactions of Batches and Their Kinetics

32. On the general role of gases as constituents in the reaction sequences of the glass melting process, from the commonly used oxidic, carbonatic, sulfatic, and other batch ingredients, either taken from natural raw materials of rock-forming minerals quarried as they are, or from products of the inorganic chemical industry, the avail-

[43] *Glastech. Ber.* **39**, (1), 11–14 (1966) (cf. II. A. ¶ 374 ff.).
[44] Vitreous Systems and Materials Yu. Ya. Eĭduk ed.), pp. 77–85, Izdat. Zinoten, Riga, 1967.
[45] *Silikaty* **13**, (4), 347–372 (1969).
[46] Cf. II.B. ¶ 39 ff. (Ch. H. Greene *et al.*, 1959.)

able literature is nearly inexhaustible. We possess a wealth of technological literature from international organizations of the glass and ceramic industries, and a rich material of excellent reports. For this reason, we may confine our selection to some of the highlights. First, we mention an outstanding report by H. Scholze.[47] We will come back to this report in subsequent works when we deal with reactions in the solid state and gas solubility in solids.

33. We emphasized repeatedly the great progress made in the field of electric fusion of glass from batches and refinement in the electric furnace. We now emphasize the importance of accurate studies of the dissolution reactions which cause the highly undesirable electrode deterioration in ac-fed furnaces, specifically the serious damage to the surface of platinum electrodes described and discussed in the literature from practical observation as reported by C. Eden.[48] The manager of glass fusion in such furnace units must be familiar with the principles and methods of electrochemical potential measurements for which the previous studies by A. Dietzel, P. Csaki, and W. Stegmaier (1940) give a full program for research and also industrially valuable suggestions.[49] The metal dispersion by *sputtering* from electrodes which disperses particles of 0.5 to 1.0 μ in diameter, is particularly essential. There are also marked correlations with the factor of changes in the basicity of the glass of the melt. Proportional to the polarization voltage one may control the sputtering effects by proper modifications in the frequency of the ac feeding the furnace, or by an additional superposition of a dc component over the ac heating system.

34. The *kinetics* of the formation of lead silicate glasses under variable conditions of the material by which Pb was introduced into the glass batch (cf. ¶ 51) may be recalled here under the aspects of investigations of such technological problems investigated by V. Gottardi, B. Locardi, A. Bianchini, and P. L. Martini[50] for different Pb oxides and their industrial brands, e.g., in their reactivity with hydrogen gas at 450°C constant, and as a function of time. Quite definite structural equilibria in the glass products could thus be established. Such studies must be of a high technological significance for an efficient selection of optimum qualities of raw materials. Their volatilization behavior in the high-temperature portions of the tank furnace (cf. Vol. II.B. ¶ 188, 208) also is important. A certain zonality in the distribution of Pb can indicate heterogeneities. The same authors[51] chose the *micro-*

[47] *Proc. Int. Congr. Glass, 8th 1968*, pp. 67–83, with excellent bibliography.

[48] In the book by E. Schott, "Beiträge zur angewandten Glasforschung," pp. 68–101, Wissenschaftl. Verlags-Ges., Stuttgart, 1959.

[49] E. Schott, Ref. 48, pp. 94 ff.

[50] *Vetro Silicati* **11**, (64), 5–11 (1967).

[51] *Glass Technol.* **9**, (5), 39–44 (1968).

hardness of the resulting Pb silicate glass from different sources in the selection of batch reactions. As a matter of fact, the microhardness was a maximum for the Si/O ratio = 0.445, coincident with a minimum in volatilization at 1270°C in the H_2 reduction effect curves. The authors concluded that for quite specific compositions the structure of the glass may have an optimum in compaction, although for the temperature conditions there are quite distinct discontinuities from case to case. For Pb–Na silicate glasses a higher ratio Si/O corresponds to maximum compaction, most probaoly as a consequence of the higher polarization effects exerted by the Na^+ ion. With increasing temperatures, such effects, however, decreasingly fade out. The particular structural arrangements existing at low temperatures could also be demonstrated in the liquid phase.

35. W. D. Johnston[52] could achieve thermodynamic equilibria for molten Na disilicate glass, in which

1.5% Ti; 1.32 to 1.68% Sn; 2.54 to 3.38% Ce; 1.54 to 1.97% Sb;
1.37 to 1.43% Mn; 1.96 wt. % Ni; 1.84% Co; 1.26 to 1.34% Va

had been added, after an exposure at 1000° to 1300°C over 1–3 days in an atmosphere composed of air, oxygen, or Ar in the ratios from 100 to 0.01; CO_2 mixed with CO in the ratios 100:1, 10:1, 1:1, 0.1:1, 0.01:1, CO_2:CO; and mixes of $H_2 + H_2O$; CO + C. The redox equilibria were studied by determination of the incremental end compositions, applying potentiometric, oxidimetric–reductometric methods (the special rotating heating systems used is shown in Fig. 7). Only the Va-containing Na disilicate melts showed disturbances by the participation of the ionic species V^{5+}, V^{4+}, V^{3+}, with stepwise redox phenomena. The redox reactions of the other systems studied are of the type.

$$2O^{2-} + 4/n\ Me^{(x+n)+} = 4/n\ Me^{x+} + O_2$$

(x the lowest valency, n the number of electrons involved in valence changes for the metal *Me*). Linear relations are valid in p_{O2} vs ($Me^+/Me^{(x+n)+}$ plots, when $n = 1$ (for all systems except the ions of Sb and Va) and when $n = 2$ for the following systems:

$$Ti^{3+}/Ti^{4+};\ Fe^{2+}/Fe^{3+};\ Ce^{3+}/Ce^{4+};\ Mn^{2+}/Mn^{3+};\ Co^{2+}/Co^{3+};\ \text{and}\ Ni^{2+}/Ni^{3+}$$

most probably, whereas for the systems

$$Sb^{3+}/Sb^{5+};\ Sn^{2+}/Sn^{4+},$$

the slopes are ±2 (cf. Fig. 8). Log k for the equilibrium constants of the single ions

[52] *J. Amer. Ceram. Soc.* **48**, (4), 184–190 (1965).

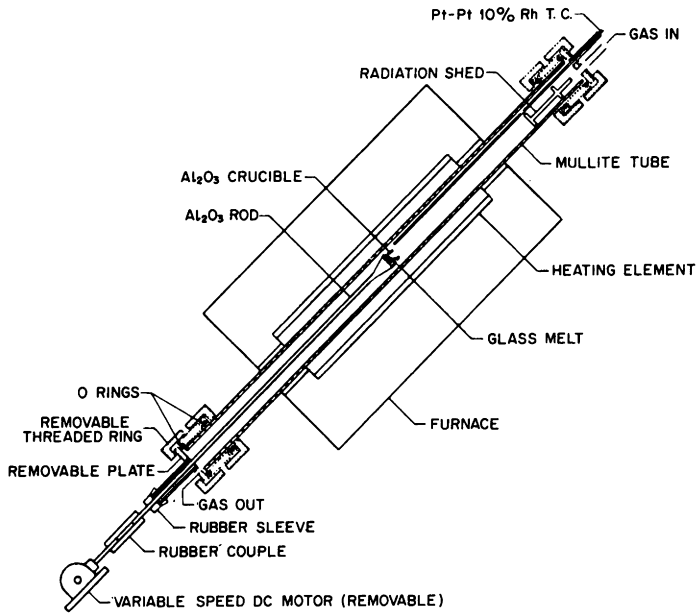


FIG. 7. Equilibrium furnace permitting rotational stirring in glass fusion in a controlled atmosphere. (Johnston.)

are directly correlated to the standard potentials equal to E_0 of the ions in aqueous solutions; log k decreases as a function of $1/T$; for elevated temperatures the concentrations of the ions of lower valences are higher. Such considerations are important for the theory of the fining of glass melts as directed by temperature effects, e.g., when Sb is used as a fusing agent, or for the effects of Sb and Co in the photosensibilization of glasses.

36. For the reduction of Fe^{3+}, Ce^{4+}, Sn^{4+} (but not for Eu^{3+}) ions in Na–Ca silicate glasses at 500°C, W. D. Johnston and A. J. Chelko[53] used analytical and spectrophotometric (adsorption) methods in the near-infrared range for a study of the diffusion mechanism of H_2, applied onto the staining of glass fibers of 15 to 50 μ in diameter and of slabs. A full discussion of the diffusion mechanism by H_2, the reducible ions acting as immobile traps was attempted. The absence of reduction effects by CO made evident in the experiments of Johnston and Chelko is a consequence of too low a product of the dielectric constant, multiplied with the constant for Henry's law ($D_g k$) in the trapping effect.

[53] *J. Amer. Ceram. Soc.* **53**, (6), 295–301 (1970).

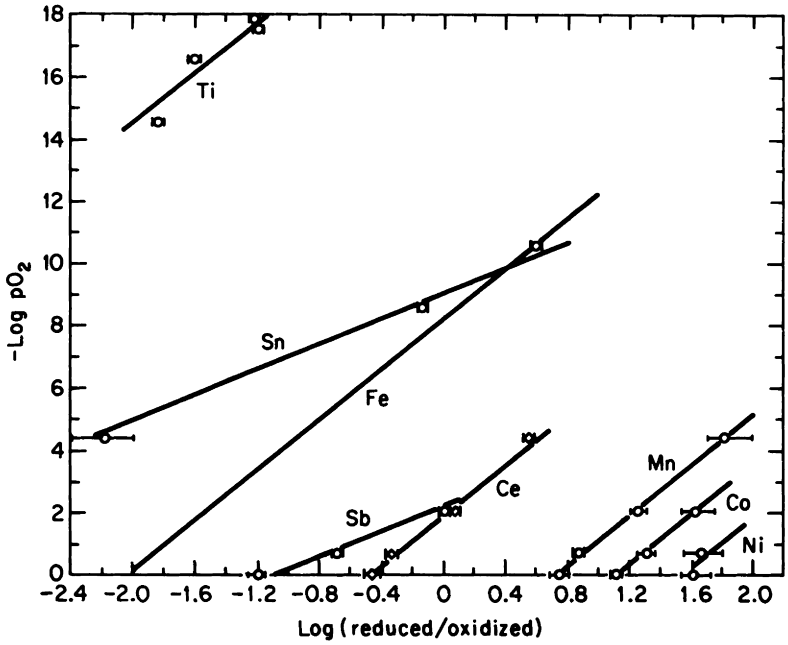


FIG. 8. Equilibrium dependence of $\log(M^{x+}/M^{(x+n)+})$ on $-\log po_2$ (Johnston.).

37. R. W. Douglas, P. Nath, and A. Paul[54] applied the mass action law for the redox conditions and the O^{2-} activity with plurivalent cations for the consideration of whether one may expect for high O^{2-} activities the lowest stage of oxidation in an oxidic glass. For Cr, Fe, and Ce, it was experimentally established that with increasing alkalinity of silicate glass composition in the transition from Li_2O to K_2O the higher valencies are preferably observed. In the same time, however, the O^{2-} activity in such a sequence can be increasing. There are apparent contradictions with the mass action theory which can be overcome according to Douglas *et al.* when the equilibrium constants change in the measure that the glass composition is changed. This could be demonstrated for binary alkali silicate and borate glasses, the basicity of which is shifted to higher amounts, whereas the O^{2-} activity is *de*creasing. Douglas *et al.* emphasize that dissolved gases (CO_2, SO_2, H_2O) in glass melts also influence the basicity, and therefore the activity (cf. Vol. II.A. ¶ 171). The reality of changes of the equilibrium constants in such cases confirms convincingly the apparent contradictions mentioned above with the mass action principles. The experimental difficulty met here is the impossibility of determining factors of O^{2-}

[54] *Phys. Chem. Glasses* **6**, (6), 216–223 (1965); cf. II. A. ¶ 177.

activity, the activities of redox ions, and the reaction constants separately. For binary alkali silicate glasses the shifts to higher oxidation states with increasing basicity can be expressed by an exponential increase of the redox ratio with the alkali contents.

GLASS FORMATION IN CARBONATE-CONTAINING BATCH SYSTEMS

38. The actual technological problem complex indicated here has been so much clarified by previous investigations on the physical chemistry of carbonate batch reactions (we recall to the extensive investigations made by C. Kröger and his school one decade ago) that we have now to refer only to some additional publications among which we particularly emphasize a Note by R. K. Datta, D. M. Roy, S. P. Faile, and O. F. Tuttle,[55] which is interesting for the revival of the old problem of pure carbonate glasses under high CO_2 pressures, e.g., in the system $K_2O-MgO-CO_2$ in which the Mg^{2+} ions play the role of the framework-forming constituents. The extension of such studies to glasses containing SO_4^{2-} and F^- anions bonded with alkaline earth cations was previously indicated in our text (cf. Vol. II.A. ¶ 1) as a contribution to the general problems of glass formation in oxidic systems.

39. M. L. Pearce[56] studied from a more technological viewpoint the solubility of CO_2 and the changes in O^{2-} activity in Na silicate glass melts by gas-analytical methods by hot extraction for concentrations of 25 to 56 wt.% over the temperature range from 900° to 1400°C. The solubility of CO_2 in such melts rapidly decreases with increasing temperatures as would be expected for the CO_2 solubility, but increases with increasing alkalinity (Na_2O concentration). As an example, in a melt with 25% Na_2O, it is only 0.001% at 1050°C, and for 56% Na_2O more than 5.0% CO_2. The reaction $CO_2 + O^{2-} \rightarrow CO_3^{2-}$ shows a direct proportionality to the O^{2-} ion activity, and this increases by four orders of magnitude in the experimental range. There is a remarkable similarity between these facts and the conditions observed by Pearce in borate glasses,[57] and for the solubility of H_2O in alkaline silicate melts.[58]

40. The results obtained by M. L. Pearce are supplemented by *radiological* measurements for the CO_2 content in melts of Na–Ca silicate glasses for different steps in the fusion process, as made by C. Kröger and D. Lummerzheim,[59] specifically for the residual CO_2 after the fining process, using C^{14} as the tracer isotope in

[55] *J. Amer. Ceram. Soc.* **47**, (3), 153 (1964).
[56] *J. Amer. Ceram. Soc.* **47**, (7), 342–347 (1964).
[57] *J. Amer. Ceram. Soc.* **48**, (4), 175–178 (1965).
[58] Cf. H. Franz and H. Scholze, *Glastech. Ber.* **36**, (9), 347–356 (1963).
[59] *Glastech. Ber.* **38**, (6), 229–232 (1965).

$BaC*O_3$ containing batches. The self-absorption effects were eliminated by dissolution of the glass (in a polytetrafluoroethylene container at 80°C) in dilute HF solution using a Friesecke–Höpfner radiation device with a high-voltage source and an amplifier. The sensitivity of this method reaches 10^{-8} g/g glass sample; the amount of residual $C*O_2$ as measured is a function of the SiO_2 content of the glass, and of the fusion temperature (cf. Fig. 9). For the kinetics ruling the carbonate batch reactions in the system $Li_2O-SiO_2-CO_2$, see M. A. Matveev and B. N. Frenkel',[60] as well as for the reactions in the solid state and the fusion process, with determination of the rate constants as a function of temperature. The importance of such studies for the fusion of carbonate batches of Na – Ca silicate glasses was demonstrated by M. Cable, C. G. Rasul, and J. Savage,[61] in combination with the control of the foaming and reboiling phenomenon, as discussed in Vol. II.B. ¶ 73 ff. 82.

41. On the *diffusion-controlled* dissolution of water in molten glass[62] in a Ca – Mg-containing Na – Ca silicate glass, L. Němec worked over the temperature range from 930° to 1180°C by the method of volume contraction of the bubbles. The mathematical treatment of such a problem and its numerical solution (cf. D. W. Readey and

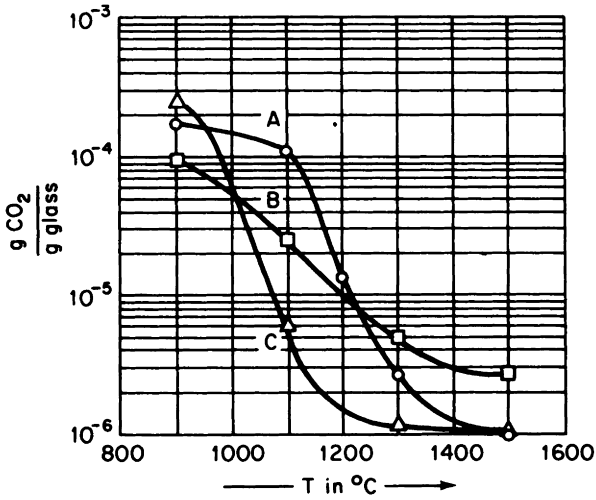


FIG. 9. CO_2 contents of glasses A, B, C as a function of the fusion temperature (melting time 90 minutes). Composition in mole %: (A) 4.85 SiO_2, 1.00 Na_2O, 1.00 CaO; (B) 3.72 SiO_2, 1.00 Na_2O, 0.71 CaO; (C) 4.85 SiO_2, 1.00 Na_2O, 0.71 (CaO. Kröger and Lummerzheim.)

[60] In the book "Glass-forming Systems and Materials" (Yu. Ya. Eĭduk, ed.), pp. 9–16, Izdat. Zinatne, Riga, 1967.

[61] *Glass Technol.* **9**, (2), 25–31 (1968).

[62] *Glass Technol.* **10**, (6), 176–181 (1969).

A. R. Cooper[63] is aggravated by the moving boundary of diffusion in the melt around the bubble, and demonstrates that the convective flow has an important influence on the apparent diffusivity which for H_2O is very high. The resulting diffusivities are of the exponential type: $D = 1.20 \times 10^{-1} \exp(-38.4RT)$. Particular attention must be paid to influences exerted by the presence of foreign gases in the bubbles on the moving boundaries, but the initial part of the observed effects of H_2O diffusivity may be sufficient to obtain reasonably accurate results. The influence of H_2O vapor on the bubble evolution when the glass melts also contain sulfates, was discussed by Kl. P. Hanke and H. Scholze.[64] Recent extensive studies on solubility and diffusivity of essential gaseous participants in the glass composition, as evolved from the batch reactions, included observations made by F. D. Lorey[65] on the so-called "secondary boiling" phenomena (¶ 87, 93, 101, 196).

42. For a certain closure of our present text on gas bubbles in glass melts, and the formation of foam glass, we add here some special publications of technological contents:

In connection with a general theory of kinetics and mechanisms of foaming glass, M. Cable[66] reports from practical experience that the bubbles decrease approximately exponentially in number per time unit during the normal fining process. The specific action of fining agents on the characteristics of those mechanisms from the batch ingredients involved here cooperates with the diffusion process of the gases into and out of the bubbles. Cable particularly gives an extensive mathematical treatment for the determination of the rise and the bursting of bubbles on the melt surface, and for their dissolution in the melt. In two other publications with C. G. Rasul[67] the effect of a "wet" furnace atmosphere above the highly undesirable "stability" of glass foams on the melt mirror is discussed in regard to the surface activity phenomena[68] on the contacts of an oxygen-containing furnace gas atmosphere, and the melt in which the presence of sulfate anions plays a very important role, in connection with the partial pressure of oxygen. The foam is not formed simply by supersaturation in the melts in respect to sulfates in the batch, in the same way as "water" is of great importance for the evolution of the foaming mechanisms.

43. V. T. Slavyanskiĭ and L. V. Aleksandrova[69] report on interesting experiments for technological production of foam glass from common Na–Ca-silicate glass, or

[63] *Chem. Eng. Sci.* **21**, 917 ff. (1966).
[64] *Glastech. Ber.* **43**, (12), 475–482 (1970); (cf. also Vol. VIII. ¶ 87).
[65] *Amer. Ceram. Soc. Bull.* **45**, (11), 1012–1013 (1966).
[66] *J. Amer. Ceram. Soc.* **49**, (8), 436–441 (1966).
[67] *J. Amer. Ceram. Soc.* **49**, (10), 568–571 (1966); **50**, (10), 528–531 (1967).
[68] Cf. H. Jebsen-Marwedel, Vol. II.B. ¶ 76 f.
[69] *Steklo Keram.* **23** (11/12), 579–583 (1966).

optical glass, to which $CaCO_3$ and SiC have been added. In the furnace atmosphere (air and N_2 under a reduced pressure of about 300 mm Hg), the heating up took place very rapidly so that within a few minutes the CO_2 evolved from the Ca carbonate raised the total pressure considerably, evidently by heterogeneous gas reactions of partial melts with SiC. For a technologically good production of foam glass the presence of SO_3 in the system is indispensable; sulfate-free optical glass does not easily foam.

44. P. Emer[70] reported on observations of spontaneous foam evolution on the batch surface of tank kilns, e.g., for glass prepared from a batch with a certain addition of phonolite for improving the fining qualities. In this case, the disturbing foam evolution was reduced by the addition of fly ash containing alkali carbonate from a Portland cement plant.

45. For the industrial production of foam glass (and so-called foam ceramics) M. Sacher[71] used a rotary kiln for the granulation of mixes of a coarse-granular soda with fine-ground quartz, limestone, and soda. The resulting spherical "granules" develop in the typical bloating process which requires a subsequent rolling of the still soft, deformable product to ribbon-shaped end products.

BOROSILICATE AND LEAD SILICATE GLASS-BATCH REACTIONS

46. H. Wessel, K. H. Schier, and P. Wange[72] recommended Na polyborates for borosilicate glass batches[73] in order to avoid normally undesirable losses in B_2O_3 in steam evolved from the batch, e.g., in the process of Pyrex glass production. Characteristic of the volatilization-impeding action of polyborates as raw materials in batches of this kind is the presence of cyclic $[B_3O_6]^{2-}$ anions, as in K pentaborate tetrahydrate)[74] for which detailed experimental examination of the dehydration mechanisms was applied, namely, differential-thermal analysis, X-ray diffraction methods, and infrared spectroscopy—in the latter case using the 3600-cm^{-1} band as an indicator of the water losses. The compound $Na_2O \cdot 3B_2O_3$ shows sharp infrared absorption signals; also its fusion point at 760°C is very distinct. Melting experiments with polyborates show a much better and smoother fusion process than the same stoichiometric mixture of borax with H_3BO_3, e.g., in the Rasotherm glass tank

[70] *Glastech. Ber.* **42**, (6), 221–228 (1969).
[71] *Sprechsaal* **102**, (17), 705–706, 710 (1969).
[72] *Silikattechnik* **16**, (1), 4–9 (1965).
[73] Cf. Corning U.S. Patent No. 2, 934, 444, April 26, 1960.
[74] Cf. W. Zachariasen, *Z. Kristallogr.* **98**, 266–271 (1937).

furnace (for this trademark glass a thermal expansion coefficient of about 100 × 10^{-7} cm/°C is combined with many desirable technological qualities).

47. An interesting recommendation is made by L. I. Sankova[75] concerning the use of concentrates of natural danburite, $CaB_2(SiO_4)_2$, as a raw material for the production of borosilicate glasses, specifically useful for the production of glass fibers. The great uniformity of such danburite concentrates which can be delivered from certain pegmatite occurrences in the U.S.S.R. is highly favorable for the production of quality glasses in this specialized field branch of glass technology.

48. The Pauly–Erdey derivatograph as a most useful control instrument for the study of batch reactions as mentioned before in ¶ 27 was also applied by G. Nölle[76] for borosilicate glass prepared from batches containing sand, soda, borax, K-feldspar, $BaCO_3$, and alumina hydrate (with addition of fluorite, As_2O_3, KNO_3 as fining agents) up to 1000°C as the reaction temperature. Corresponding studies were made by W. R. Ott and M. G. McLaren[77] who developed a complete thermodynamic analysis of the reactions for the formation of Pb silicates, including a heat balance calculation for related technological systems.

49. Combined lead silicate, and Ca–Na borosilicate glass batches were studied by V. Gottardi, B. Locardi, and G. Bonetti,[78] concerning the reactivity of mixtures containing α-PbO (lithargo), in the transformation temperature range. Theoretically, such a reaction is interesting for the manner in which PbO and B_2O_3 influence the coordination (prevailingly coordination number = 3) of B^{3+} in the resulting glass. The reactions as such advance over an intermediate formation of Pb borates which then, in a second stage are dissolved in the final glass phase. Such a reaction type can be neither compared nor theoretically interpreted by the classical reaction kinetics of solid–solid mixtures, nor with reactions of simple dissolution of crystalline phases in the glass liquid. They are correlated to the surface structure of the intermediate glasses, specifically ruled by the glass composition as such, and changes in temperature. Interesting color changes from red to yellow might indicate different reaction sequences and mechanisms for PbO as the α-PbO phase (tetragonal, red lithargo) and β-PbO phase (orthorhombic, yellow massicot). The assumption of simple polymorphic inversions, however, is not confirmed by X-ray diffraction analysis, by which no crystalline phases at all could be identified.

50. Concerning the important differences in the meaning of so-called "*melting*

[75] *Steklo Keram.* **23**, (7/8), 379–380 (1966).

[76] *Wiss. Z. Hochsch. Architekt. Bauw. Weimar* **13**, 601–604 (1966).

[77] *Proc. Int. Conf.* Thermal Analysis, 2nd, Academic Press, New York, 1969; *Mettler Techn. Bull. T.* **108**, 5 pp. (1965) with many instructive diagrams, concerning the Mettler Thermoanalyzer.

[78] *Vetro Silicati* **9**, (5), (53), 6–9 (1965).

history" effects for the physical-chemical properties and the general behavior of glasses, we may here recall the *structural aspects* which C. L. McKinnis and J. W. Sutton[79] had suggested. More recent observations are chosen and reported by G. E. Rindone[80] on the same subject, and valuable newer experience from the manufacture and testing of glass fibers are reported by N. M. Cameron,[81] particularly on the behavior of different glasses in the silver stain process as studied by V. Gottardi and B. Locardi.[82] Here quite evidently, structural changes as a function of the "melting ages" are emphasized, particularly by Rindone. We return to this very peculiar and not quite easily examined field again later when the question of how to interpret "posthumous" homogenization tendencies and reaction in glass arises (cf. Vol. II.A. ¶ 302).

51. Starting from the Gibbs–Helmholtz equation and the methods of N. A. Landiya,[83] G. M. Matveev and G. B. El'kin[84] presented a complete tabulation of equations and numerical data for the system $PbO-SiO_2$ over the temperature range from 298° to 1800°K, which illustrates the stability conditions of the compounds also depending on their ratios PbO/SiO_2 and the heats of fusion. They also presented graphs for the practical determination of the efficiency devices and methods used for industrial lead glass production. The *rates* of the formation of different lead silicates in glass batches, with particular respect to "individual" properties of different PbO raw materials in a batch for a K–Pb crystal glass, became particularly striking when, as a basis of comparison for the different materials, the reducibility of PbO by hydrogen gas was tested, which parallels the differences in the reactivity of such samples with other batch constituents. Such differences are of equally great practical importance and are theoretically significant when problems of structural differences in the batch reaction products are in question; this means in the kinetics of batch reactions. These observations and other experiments studied by V. Gottardi, B. Locardi, A. Bianchini, and P. L. Martini[85] made evident typical "thermal history" effects in the samples. Figure 10 shows an impressive diagram with the results of nine differently treated PbO raw materials, demonstrating their reducibility by hydrogen at the test temperature of 450°C in very strikingly different curves for the reactivity

[79] *J. Amer. Ceram. Soc.* **42**, 194–199 (1959); **42**, 250–253 (1959).

[80] *Silikattechnik*, **19**, (8), 246–250 (1968).

[81] *J. Amer. Ceram. Soc.* **49**, (3), 144–148 (1966).

[82] *Phys. Chem. Glasses* **5**, (5), 137 (1964).

[83] "Calculation of High-Temperature Heat Capacities of Inorganic Compounds by Standard Entropies Data," Izdat. Akad. Nauk Gruz. SSR., Tiflis, 1962; see also H. Benz and H. Schmalzried, *Z. Phys. Chem. N.F.* **29**, (1/2), 77–82 (1961).

[84] *Silikattechnik* **20**, (7), 225–227 (1969).

[85] *Vetro Silicati* **11**, (4), (64), 5–11 (1967).

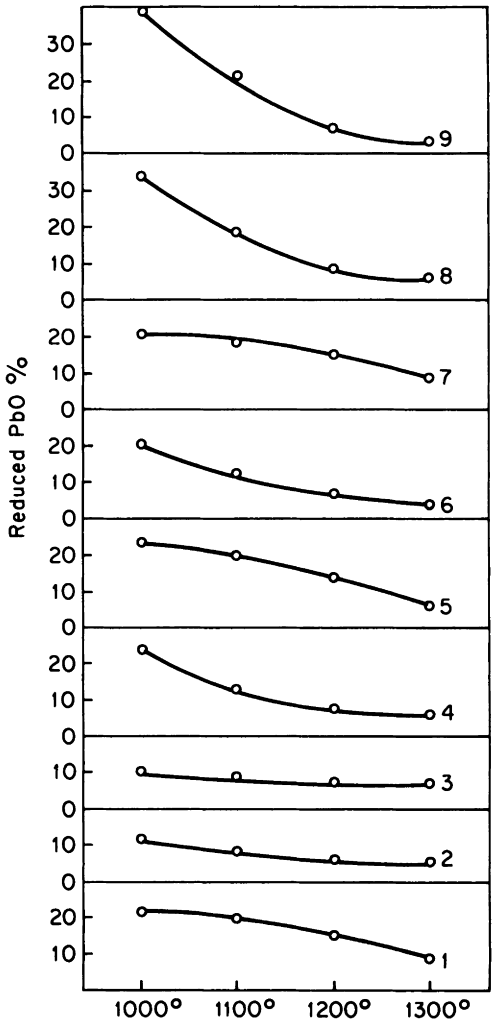


FIG. 10. Nine lead silicate glasses of theoretical composition 25% PbO, 15% K_2O, 60% SiO_2, and molten at temperatures over the range from 1000° to 1300°C using different lead compounds (see below) as raw materials. The curves indicate the different degrees of reduction of the lead oxide by reaction in a current of hydrogen at the constant temperature of 450°C. (Gottardi, Locardi, Bianchini, and Martini.)

Note: raw materials of the single glass samples were: (1) Massicot; (2) Litharge; (3) Calcinated massicot; (4) Calcinated basic Pb carbonate; (5) Minium, treated with dilute HNO_3; (6) Minium; (7) Synthetic cerussite, $PbCO_3$; (8) Precipitated basic Pb carbonate; (9) Pb nitrate.

of those materials in the batches for a K – Pb silicate glass as a temperature function (between 1000°C and the equilibrium temperature of 1300°C). Experiments aimed to demonstrate the different nonequilibria of those diversified oxide materials by volatilization determinations at high temperatures have not had, so far, such convincing results.

SULFATE REACTIONS IN GLASS BATCHES

52. Mutual oxidation and reduction processes in equilibria are of great importance in glass technology, particularly because of their gaseous reaction products and the formation of sulfite and sulfide anions (of tetravalent and divalent sulfur). The phenomena most commonly combined with such reactions are striking staining effects in the resulting glasses, namely the widely occurring phenomena of "coal-yellow" or "amber" glass formation, when traces of iron are found in the glass raw materials. S. M. Budd[86] studied these processes in view of correlations of sulfite in combination with sulfide, but never of sulfate and sulfide, with a considerable reduction in sulfur "solubility" when the oxidation level is decreased. Sudden changes in the oxidation level of glass exerts influence also on the release of sulfur in the gaseous phase.

53. The system $Na_2O - SiO_2 - Na_2SO_4$ at the experimental temperature of 1200°C was investigated by M. L. Pearce and J. F. Beisler[87] specifically in respect to the region for two liquid phases in equilibrium (cf. Fig. 11) which is in relatively good agreement with the results of previous studies made by E. Kordes, B. Zöpelt, and H. J. Pröger.[88] The conjugation (tie-) lines which converge to the apex point for practically pure Na_2SO_4 (solubility of silica in Na_2SO_4 is about 0.1 wt.% at 1200°C), but the two-liquid field (miscibility gap) does not extend to higher Na_2O/SiO_2 ratios above 1.0. Some smaller deviations from data of Kordes' *et al.* may be due to slight contaminations of the melts by Al_2O_3 which was dissolved from the refractory material of the fireclay crucibles used. More surprising perhaps is that Kordes *et al.* did not indicate in their phase diagram for the melt equilibria of the system $Na_2O - Na_2SO_4 - SiO_2$ a rather extended field for the coexistence of two liquid phases with silica (as tridymite). Nevertheless, the equilibrium conditions in an open system as studied by Pearce and Beisler postulate a consideration of the heterogeneous gas reaction $SiO_2 + SO_4^{2-} \rightleftharpoons SiO_3^{2-} + SO_3$, which describes the desulfurization reaction of the glass melt in the fining stage.

[86] *Bull. Amer. Ceram. Soc.* **44**, (4), 405 (1965).
[87] *J. Amer. Ceram. Soc.* **48**, (1), 40–42 (1965).
[88] *Z. Anorg. Chem.* **264**, (5/6), 255–271 (1951).

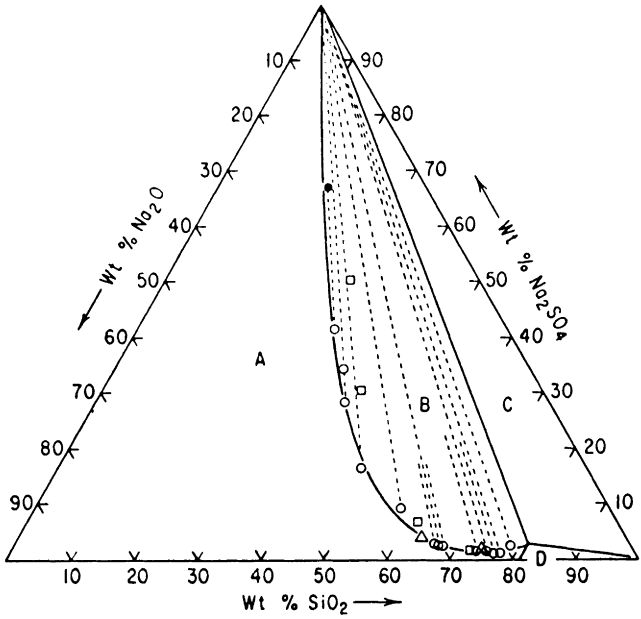


FIG. 11. Miscibility gap in the system $Na_2O-Na_2SO_4-SiO_2$ at 1200°C (isotherm). (Pearce and Beisler.) Liquid phase in Area A; two liquid phases in Area B; area C corresponds to coexistence of two liquids with tridymite; area D to that of one liquid with tridymite.

54. In the light of highly analogous metallurgical reactions in the type of sulfate–ferrite metallurgical processes, as studied by P. Grieveson and E. T. Turkdogan[89] the extension of the miscibility gap depends on the framework-forming properties of SiO_2 as the acidic oxide and the framework-modifying properties of the basic oxide. The discussion of such analogies would predict, e.g., for a substitution of SiO_2 by Al_2O_3 in the system $Na_2O-Na_2SO_4-SiO_2$, because of the limited framework-forming nature of Al_2O_3, a reduction of the two-liquid field in Fig. 11 as shown above. Some data among the observations of Kordes *et al.* evidently confirm this conclusion sufficiently. A calculation of the activity coefficient for Na_2SO_4, namely, of log $\gamma^0_{Na_2SO_4}$, as a function of the relative content in Na_2O in the melt composition shows an unusually high value for this coefficient, and a sharp maximum of the ratio $Na_2O/SiO_2 = 0.22$. Also, this fact is analogous to what is observed in the systems $Na_2O-Na_2SO_4-Fe_2O_3$ and $CaO-CaSO_4-Fe_2O_3$.[90]

[89] *Trans. Amer. Inst. Metallurg. Eng.* **224**, 1086–1095 (1962).

[90] See also E. T. Turkdogan and L. S. Darken *Trans. Amer. Inst. Metallurg. Eng.* **221**, 464–474 (1961); E. T. Turkdogan and P. Grieveson, *ibid.* **224**, 1086–1095 (1962).

55. The glass-forming system $K_2O - K_2SO_4 - SiO_2$ is in its equilibrium conditions for 1300°C, according to E. Raask and R. Jessop[91] rather similar to that of the $Na_2O - Na_2SO_4 - SiO_2$ diagram discussed above. Also similar is the high value of the activity coefficient log $\gamma^0_{K_2SO_4}$, with a maximum at $K_2O/SiO_2 = 0.13$ for the molar fraction. Observation of the mixing process and the behavior of the two-liquid phases in droplets under the heating microscope is particularly instructive.

56. An extensive calculation of the activities for Na_2O in molten Na_2So_4 and Na silicate melts was presented by St. Holmquist.[92] For the thermal decomposition of Na_2SO_4 the reaction constant $K = [Na_2O] \cdot p_{O_2}^{1/2}$ could be calculated from available thermodynamic data and approximated by the equation $\log K = 11.9 - 3.38 \times 10^4/T$, tabulated and plotted for the temperature range from 800° to 1450°C. Also for the activity for Na_2O in Na silicate melts in equilibrium with Na_2So_4 and in $SO_2 + O_2$ atmosphere at 1200°C see Fig. 12 which gives a plot of the results of Holmquist, in comparison with those of M. L. Pearce[93] for $Na_2O - Na_2SO_4 - SiO_2$, and $Na_2O - Na_2CO_3 - SiO_2$, with differences by nearly three orders of magnitude. An explanation of this surprising difference may be given according to Holmquist by the tacit

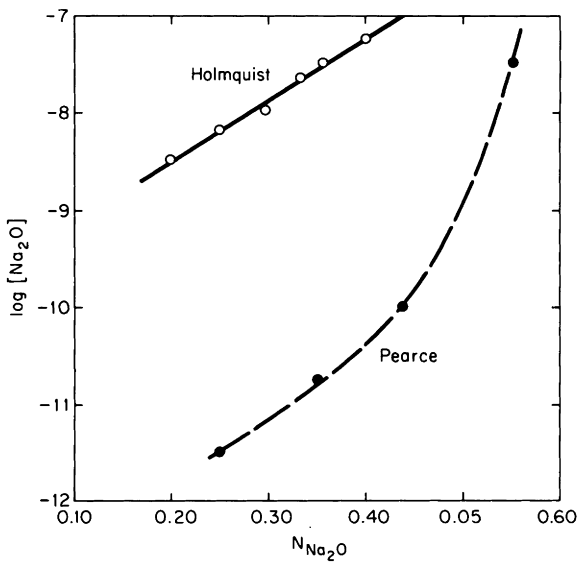


FIG. 12. Sodium oxide activity in sodium silicate melts at 1200°C, plotted as log (Na_2O) vs. mole fraction N_{Na_2O}. (Holmquist.)

[91] *Phys. Chem. Glasses* **7**, (6), 200–201 (1966).
[92] *Phys. Chem. Glasses* **9**, (1), 32–34 (1968).
[93] *J. Amer. Ceram. Soc.* **47**, (7), 342–347 (1964); **48**, (12), 611–615 (1965).

assumptions made by Pearce that the carbonate anions in Na silicate melt solutions would behave "ideally"; this can no longer be upheld.

57. Holmquist[94] extensively calculated the thermal reaction data for Na *sulfite* and silica in batches. In view of strongly contradictory observations found in the literature, it was observed that from such a sulfite–silica melt, between 700° and 900°C, Na_2SiO_3 and *free* sulfur are evolved apparently in a succession of steps. Na sulfate reacts with free Si to evolve free sulfur at 750°C. The interpretation of the amber staining and the presence of Na_2SiO_3 is substantiated. Specific studies by Holmquist of the oxygen activity and the solubility of SO_3 in the Na silicate melts[95] in the range from 1150° to 1250°C in the equilibrium with gas mixtures of SO_2 and oxygen were interpreted by a linear function and equation

$$\log(SO_4^{2-}) = \log(p_{SO_2} p_O^{1/2} + \log Y$$

in which Y is a function of the ratio Na_2O/SiO_2. A series of nearly parallel lines for these various ratios could be obtained for the reactions at 1200°C. Relative free oxygen activities calculated for this temperature are in good agreement with theoretical values derived from the G. W. Toop and F. S. Samis thermodynamic model[96] which is developed for equilibrium relations between bridging and non-bridging and free O^{2-} ions.

COMPOSITION AND REACTIONS OF THE GLASS TANK FURNACE ATMOSPHERE

58. The successful mobilization and performance of the *gas-chromatographic method* for the investigation of glass-batch reactions is very well illustrated by the experimental work of P. Heyndryckx and D. Bonnan[97] for a complete replacement of the classical Orsat gas-analytical automat by an entirely modernized instrumentation. In principle, the task of such improved devices is to separate solute distributions in several mobile (fluid) phases in a continuous flow system by an adequate combination of columns and detector arrangements. For the gas sampling from the furnace atmosphere, however, silica glass tubing cannot be used because it is permeable for CO. One may substitute the silica glass by stainless-steel tubing to conduct the CO_2, SO_2, SO_3 mixture into copper tube columns filled with *n*-dioctyl phthalate or hexadecane over acid-washed "Chromosorb W" (Johns Manville product). Absorption of H_2, O_2, N_2, CH_4, and CO is conducted over 13A molecular sieve

[94] *Glass Ind.* **47**, (10), 558–559 (1964).
[95] Cf. *J. Amer. Ceram. Soc.* **49**, (9), 467–473 (1966).
[96] Cf. *Trans. AIME* **224**, (5), 878–887 (1962); *Can. Met. Quart* **1**, (2), 129–152 (1962).
[97] *Verres Refract.* **21**. (2), 82–87 (1967).

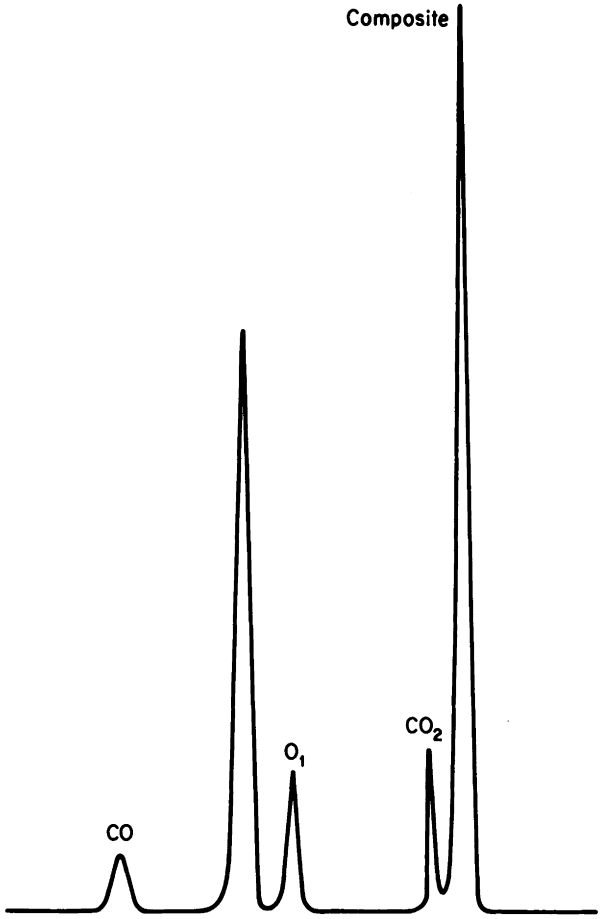


FIG. 13. Gas-chromatographic diagram of the gas composition in a glass furnace atmosphere. (Heyndryckx and Bonnan.)

zeolite (faujasite type) of about 250-μ granular size. A heat conductance cell with thermistor is used as a detector. Helium is used as the inert carrier gas. Figure 13 shows an example of gas-chromatographic diagrams obtained. The peaks in the detector signal spectra for the single gases are recorded and evaluated by determination of the peak areas, either by an electromechanical integrator or by planimetry. The methods are described by Heyndryckx and Bonnan in their general applicability for the continuous furnace control in glass production also for the analysis of the gaseous contents of bubbles evolved in the fining process,[98] as shown in the

[98] See Heyndryckx and Bonnan, *Verres Refract*, **21**, (3), 196–198 (1967).

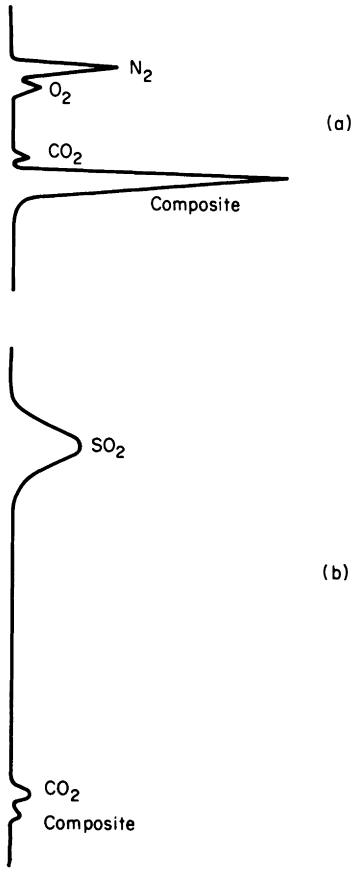


FIG. 14. Gas-chromatographic diagrams showing the gas composition of two typical fining bubbles (a) and (b) (Heyndryckx and Bonnan).

diagram Fig. 14, giving an example for the latter case. Changes which take place during the fining period in the composition of these gases in bubbles are of great significance for the correct evolution and operation of the fining process (cf. ¶ 79 ff.).

59. *Mass spectrometric* analysis of gases evolved in the decomposition of alkali metal sulfate in glass batches are the subject of investigations by P. J. Ficalora, O. M. Uy, D. W. Muenow, and J. L. Margrave.[99] The high-temperature equilibrium vapor species observed in the mass spectrometer are, besides the alkali metal mole-

[99] *J. Amer. Ceram. Soc.* **51**, (10), 574–577 (1968).

cules themselves, those of O_2 and SO_2, but also those of the sulfates, the mobilization of which is more important the heavier the alkali metal sulfates. Thermodynamic data could be applied for a calculation of the enthalpies of the sulfate decomposition, and the heats and entropies of sublimation. For further data on the existence of free Na_2O and Li_2O in the gaseous form, as L. Brewer and J. L. Margrave[100] in previous studies had fully confirmed by mass spectrometry, cf. J. Berkowitz, W. Chupka, G. D. Blue, and J. L. Margrave[101]; D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linesky.[102]

60. Of more direct interest for glass-technological conditions, are investigations made by H. Meier zu Köcker and J. Brandt.[103] The apparatus used for such experiments makes possible the rapid analytical determination of N_2, O_2, and SO_3 in the gases, the correlation to the sulfur content of the fuel oil and of the heating system of the furnace, and their interaction with the glass melt surface. Special methods were elaborated for the control of sulfite and sulfate formation by heterogeneous gas reactions in the furnace atmosphere immediately above the glass melt surface. However, only the gravimetric determination of SO_2 and SO_3 in the glass could reliably gauge the absorption of sulfur in the glass, and in combination with the SO_2 and SO_3 content in the combustion gas atmosphere. In their second publication mentioned above, the authors evolved special methods for the calculation of the important role of the sulfur content of the fuel oil, in general, and for the reaction balance of the tank furnace operation, in neutral, or slightly reducing gas atmospheres, in connection with conditions for the development of sulfate in distinct formation and condensation zones. Together with a microscopic and X-ray diffraction control of the crystalline reaction products, it was actually possible to establich conclusive rules for the furnace conduction required to eliminate the undesirable formation of glass gall ("sulfate water"), which the instructive micrographs demonstrated.

61. In a third publication H. Meier zu Köcker and Dh. Ch. Roy[104] discussed new experiments with the time-dependent *reactive absorption of* SO_3 into glass melts of Ca–Na silicate composition, as a function of concentration profiles in SO_3 from an artificial furnace combustion atmosphere. They used a light *fuel oil* which had been adjusted (by introduction of the sulfur in the form of carbon disulfide, to a constant concentration of 4.6%, at a temperature of 1160°C, and an air consumption

[100] *J. Phys. Chem.* **59**, (5), 421–425 (1955).
[101] *J. Phys. Chem.* **63**, 644–648 (1959).
[102] *J. Chem. Phys.* **39**, (10), 2463–2473 (1963).
[103] *Glastech. Ber.* **42**, (5), 186–192 (1969); **42**, (7), 284–290 (1969).
[104] *Glastech. Ber.* **45**, (4), 139–146 (1972).

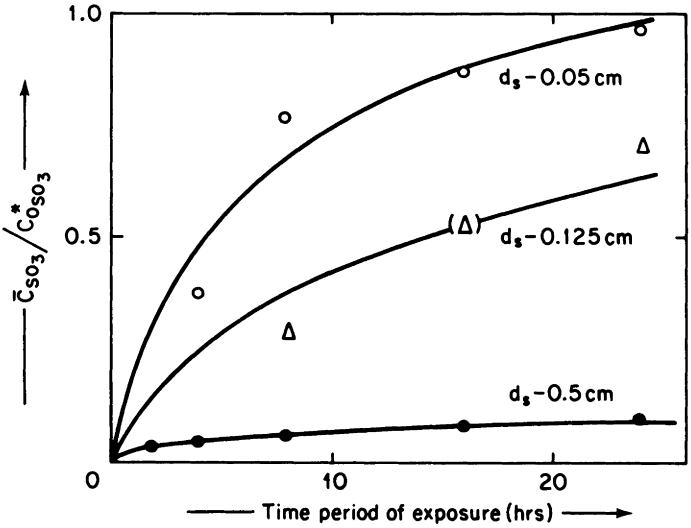


FIG. 15. Correlation of the standardized concentration in sulfate with the exposure time period for variable layer thicknesses. (Meier zu Köcker and Dh. Ch. Roy.)

ratio of $\lambda = 1.2$) over periods of 4–24 hours. The results show variations in the final SO_3 concentration by about 15%, defined for a final concentration in a thin surface skin of the glass melt ($d_s = 0.05$ cm). A theoretical derivation of cooperative diffusion and convection effects for the solubility of SO_3 could be presented by Ph. Ch. Roy based on an elementary plate model concept.[105] The curves shown in Fig. 15 for the functional correlation existing between normalized SO_3 concentrations and the time period of surface action show a good agreement with the theoretical calculation results, for different absorption layer thicknesses, d_s in cm, and a direct proportionality with the Fourier numerical ratio $Fo = Dt/d_s^2$ (D is the diffusion coefficient), from which the diagram Fig. 16 was derived. (cf. Vol. II.B. ¶ 80 ff., 86 ff.).

62. In a certain parallel to the problems of sulfur volatilization from glass batches by heterogeneous gas reactions, is the practically important question of the origin of losses of *selenium* from batches of industrial Se ruby glass for which Z. Karch[106] disclosed extensive theoretical premises. Elementary Se reacts rapidly with soda in the batch to form sodium selenite, Na_2SeO_3, associated with Na_2Se,

[105] Cf., Dh. Ch. Roy, Inaugur. Dissertation, Tech. Univ., Berlin, 1971; for the mathematical methods applied cf. J. Crank, "Mathematics of Diffusion," Oxford Univ. Press (Clarendon), London and New York, 1967.

[106] *Sprechsaal* **99**, (9), 368–374 (1966); see also Szklo Ceram. **17**, (6), 144–149 (1968).

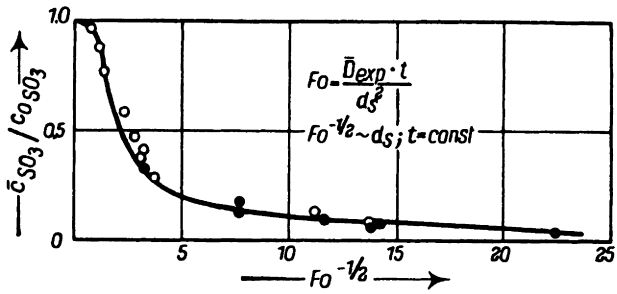


FIG. 16. Functional correlation of sulfate concentration and layer thickness, expressed by the Fourier index (*Fo* and $Fo^{-1/2}$). (Meier zu Köcker and Dh. Ch. Roy.)

followed by a reaction of the selenite with silica to evolve SeO_2. In an atmosphere containing CO by reduction, Se is evolved. Again in the presence of CO_2 and CdS, which is commonly added to glass batches of Se ruby glass (to make certain corrections in the ruby color), Se is evolved. Finally, a direct disproportionation of the alkali selenite plus selenide takes place to again form Se in the elementary form. Strongly acting reduction agents like free carbon may increase the persistence of selenide in the Se ruby chromophore, without any increase in volatilization of Se by intermediary soda reactions. In contrast with other hypotheses, ZnO, added to ruby batches, does *not* participate anyhow in the reduction to free Se. On the other hand, Na_2SeO_3 is thermally rather stable up to 1200°C but with silica it is rapidly decomposed to evolve Se vapor at about 900°C. The observations of Karch are in a high degree confirmed by more recent observations made by M. Boffé, C. Dupont, and G. Letocart,[107] of which we briefly reported in Vol. VI.C. ¶ 161, footnote 281; more details are available in this volume, ¶ 161 and 193.

63. Experimental studies of the applicability of X-ray fluorescence analysis to the study of glass formation problems have not been lacking in recent years, but for elements with atomic numbers below 22 (Ti as the upper limit) the results were not particularly encouraging. The physical conditions for CrKα radiation primarily for the excitement of fluorescence have been discussed from the viewpoint of elementary analysis in glass production materials as a control, by M. Folloni,[108] but P. Heyndryckx and J. Chenebaux[109] have indicated that a not inconsiderable improvement of the efficiency and reliability of X-ray fluorescence analysis is possible when quite specialized corrections are applied. We may add to these remarks, in spite of their not yet satisfactory results concerning quantitative analytical data, essential

[107] *Szklo Ceram.* **17**, (8), 240–244 (1967).
[108] *Verres Refract.* **22**, (5), 480–495 (1968).
[109] *Verres Refract.* **26**, (2), 45–52 (1972); *Silicates Ind.* **35**, (2), 37–42 (1970).

contributions by M. Schneegans[110] of the details of theory and proposals for the correction and elimination of disturbing matrix effects in fluorescence analysis. It would be helpful to consider the fundamental derivation of fluorescence X-ray intensities from mixtures as disclosed by J. Sherman[111] and R. Tertian[112] for an orientation.

64. The high degree of efficiency one may expect from X-ray fluorescence methods and secondary emission—in spite of the intrinsic difficulties indicated above—is, in many respects, not reason enough to overlook direct proof given for its high elegancy when applied in glass research and technology. P. Heyndryckx and J. Chenebaux[113] again gave full evidence of such substantial possibilities in a special study of diffusion radiation as an inner standard for the determination of small amounts of Se and Sr present in glass raw materials after elimination of influences exerted by matrix effects. In this particular case, it was possible to determine Se (calculated as SeO_2) in concentrations of 0.001 to 1.00%, and Sr (calculated as SrO) between 0.3 and 1.5%, with limit errors of ±10%.

DISSOLUTION PROCESSES OF SOLID BATCH INGREDIENTS

65. Of eminent practical importance is an accurate knowledge of the chemical reactions and physical conditions for the dissolution mechanism of solid (crystalline) batch constituents, primarily of quartz (as sand), limestone, dolomite, and other raw materials. H. Jebsen-Marwedel and W. Buss[114] used the heating microscope to obtain excellent micrographs of most characteristic details in such processes to demonstrate *ad visum* the important influence of different grain sizes and shapes of such materials. They also show the role of additions like Na_2SO_4 for the control of highly undesirable agglomerations of fine-granular material in the batches during the progressive liquefaction in the pile, the wetting of the grain surface, and the appearance of phase heterogeneities which may appear surprisingly mechanically resistant up to relatively high temperatures to create anomalies in the fining operation. The technical mastership of the authors of the microphotographic studies is to be appreciated highly.

66. J. Löffler[115] studied in a similar manner the diffusion effects between quartz grains and the glass melts in advancing stages of homogenization, the dynactive (after

[110] *Verres Refract.* **24**, (3), 133–140 (1970); **24**, (4/5), 185–214 (1970); **24**, (6), 242–250 (1970); Thése. Univ. Paris, April 5, 1968.

[111] *Spectrochim. Acta* **7**, 283–306 (1955).

[112] *Philips Publ.* **1**, 1–14 (1964).

[113] *Vetro Silicati* **12**, (6), (72), 5–13 (1968).

[114] *Sprechsaal* **95**, (9), 199–212 (1962).

[115] *Glastech. Ber.* **36**, (9), 356–370 (1963); **36**, (11), 452.

Jebsen-Marwedel) phenomena on the contacts between different phases in the batch pile, and stages of the fining process, by highly impressive interferometric evidence in the detection of heterogeneities, and the development of cords (striae). Mostly, sand grains are not directly dissolved as such, but undergo an inversion from quartz into cristobalite which then reacts with the alkaline silicate melt spreading over the glass surface with dynactive phenomena, thus promoting a flow circulation to smooth out contrasting differences of chemical composition in the melt phases. The rates of such processes may vary from grain to grain in the melting-down of the batch pile.

67. Interferometric measurements combined with electron microscopic and electron-beam microprobe analyses from point to point, as demonstrated by E. W. Sucov and R. R. Gorman,[116] pursue the Ca diffusion during the dissolution of limestone and dolomite in the batch mixes, the activation energy of which can be determined with essential results and conclusions. In this investigation, full evidence was given of how Ca^{2+} cations and O^{2-} anions migrate simultaneously in the diffusion flow preserving electroneutrality under given concentration gradients. The electron microprobe data distinctly speak in favor of a counter diffusion of Si^{4+} in the opposite direction.

68. Such observations may also be understood from investigations made by H. Scholze and E. Galanulis[117] on the dissolution of limestone and dolomite grains from batch mixes by reaction with early melts, in a certain degree supplementing the previous observations of Jebsen-Marwedel and Buss (¶ 65). It is most remarkable that at 1200°C a change in the viscosity versus temperature correlations must take place, namely a reversion of this function to an accelerated decrease of the influence of temperature with increasing fluidity of the melts, thus promoting dissolution and homogenization. The threshold temperature is known from simple observation of the fusion process in the behavior of the melt batch of common Na–Ca silicate flat glass, as a rather sudden change of flow conditions in the tank furnace. Scholze and Galanulis observed that the dissolution of *dolomite* granules is completed at lower temperatures than that of limestone particles. Even when it is difficult to establish a fully satisfactory mathematical evaluation of such facts and findings, the product of diffusion coefficient and time is of decisive importance for the practical survey of the fusion process. We also recommend, with G. Dusollier and J. Robredo,[118] the application of a microdevice for differential-thermal analyses of glass to survey the role that slight concentrations of incidental contaminations may play, with the properties of industrial special

[116] *J. Amer. Ceram. Soc.* **48**, (8), 426–429 (1965).
[117] *Tonind. Z.* **90**, (4), 145–146 (1966).
[118] *Verres Refract.* **21**, (6), 550–554 (1967).

glasses, e.g., those for high infrared-transmissivity characteristics[119] (cf. ¶ 103), on the dissolution of graphite electrodes in electrical furnace melts, or of "vitreous carbon," and different qualities of refractory crucibles indispensable for the manufacture of such glasses[120] among which purest sintered alumina is still the best.

69. Returning to typical problems of glass manufacture we emphasize as an excellent study of the dissolution behavior of quartz (polished spheres of 2.00–2.84 mm in diameter) in an alkali silicate melt, that by K. G. Kreider and A. R. Cooper,[121] with an elaborate mathematical analysis, taking into account the migrating boundary conditions in such a system (cf. ¶ 41, footnote 63). In this nearly model experiment, it was established that dissolution is a molecular diffusion reaction, with the diffusion coefficient 4.4×10^{-8} cm^2/second at 950°C, for a silicate melt with 40 wt. % Na_2O. Larger spheres are distinctly dissolved with a higher speed than are the smaller ones, which may be interpreted as an effluence of density and convection factors. This latter variable, however, can be eliminated in the calculation operation when the numerical results and experimental data are extrapolated to $r = 0$. We also recall the very valuable studies on the dissolution of silica glass rods in sodium melts by M. Truhlářová and O. Vepřek[122] under the same aspects.

70. A. Packter[123] studied the kinetics of the heterogeneous reaction of silica with melts of different alkali salts (halogenides, hydroxides, carbonates, sulfates) which are important not only for the interpretation of batch melting but also for the dressing of metal ores, the corrosion of refractories, and the slag formation in metallurgical processes (e.g., the corrosion slagging of refractories). For such diversified reactions the overall kinetic equations after L. Reed and L. R. Barrett[124] could be applied, and the rates of interaction calculated, including the activation energies.

71. The sphere dissolution method of Kreider and Cooper (see above) was more recently repeated for quartz spheres of only 0.3 mm diameter, by J. Hlaváč and H. Nademlýnská,[125] at 900° to 1200°C; graphs (cf. Fig. 2 in ¶13) are demonstrated to represent the relative radii a/a_0, as a function of the dissolution time and of a_0^2. Most probably the results can be interpreted as representing molecular diffusion conditions for the dissolution rates. The effective diffusion coefficients are in the order of magnitude between 10^{-7} and 10^{-8}cm^2/second. The activation energies are negligible for silica glass and quartz.

[119] Cf. the experience of F. Pernot and C. Kojima, *Verres Refract.* **20**, (5), 343–353 (1966).
[120] *Verres Refract.* **20**, (3), 189–196 (1966).
[121] *Glass Technol.* **8**, (3), 71–73 (1967); **9**, (1), 21 (1968).
[122] *Glastech. Ber.* **40**, (7), 257–260 (1967).
[123] *Silicates Ind.* **33**, 341–345 (1968).
[124] *Trans. Brit. Ceram. Soc.* **63**, (10), 509–534 (1964).
[125] *Glass Technol.* **10**, (2), 54–58 (1969).

72. Important contributions to the problems of dissolution of silica in the modification of cristobalite (in the shape of polycrystalline rods of 2 mm diameter) in a series of low-alkali borosilicate glasses (with 0 to 10 wt % Na_2O, and the atomic ratios Si/B = 1.73) above 1300°C came from E. F. Riebling[126] (cf. ¶ 14) together with a comparison of silica glass and quartz rods, heat treated in the same way above 1250°C, i.e., extensively inverted into cristobalite. It is particularly emphasized that Riebling drew conclusions from the results of laboratory experiments on the dissolution situation. In the industrial tank furnace, convective flow actions of the melts are of essential significance, when numerous thermal, composition, and velocity gradients cooperate in the dissolution mechanisms whereas, in laboratory experiments, for the desirable reproducibility of data, mostly all gradients of that kind are to be eliminated. The translation from the conditions of the experiments onto those of the industrial glass fusion process is therefore difficult; flow conditions in the industrial process accelerate the reactions and homogenization. This is also valid for a comparison with the results of previous similar experimental series in which the conditions of reaction-determining gradients prevailed, when e.g., H. W. Samaddar, W. D. Kingery, and A. R. Cooper[127] applied a controlled rotation of the entire reaction dissolution system (solid + melt) at a constant speed, not only for silica, but also for alumina, mullite, and anorthite reacting with *slag* melts (cf. Vol. II.C. ¶ 76, footnote 121).

73. Castaing's method of the electron-beam microprobe analysis (cf. Vol. VI.C. ¶ 213 ff.) is a particularly efficient and valuable instrument, not only for the study of dissolution processes in glass batch melts, or corrosion phenomena with ensuing formation of striae (cords) in the finished glass products as the most frequently observed defects by heterogeneities, but also as a quantitative-analytical method in the microareas of a few μ^2 sizes. We therefore recommend for a study of the recent literature in this important field of glass technology, the following few publications of a high value for practical application, with characteristic examples of method instrumentation, and results from and for the practice:

R. V. Adams, H. Rawson, D. G. Fisher, and P. Worthington,[128] with demonstration of instructive material from glass manufacturing, and of anomalies and defects in glass samples (cf. Vol. II.B. ¶ 187, 203);

T. N. Brock and E. D. L. Carter,[129] specifically on the examination of cords in Na – Ca silicate glass, in many details corresponding to J. Löffler's and S. Tolansky's interferometric investigations (cf. Vol. II.B. ¶ 186 ff.);

[126] *Amer. Ceram. Soc. Bull.* **48**, (8), 766–769 (1969).
[127] J. Amer. Ceram. Soc. **47**, (5), 249–254 (1964).
[128] *Glass Technol.* **7**, (3), 94–105 (1966).
[129] *Amer. Ceram. Soc. Bull.* **45**, (6), 574–577 (1966).

74. J. P. Hazart and E. Weinryb[130] who reported particularly on a wealth of experience in the application of the electron-beam microprobe for detection and studies of the chemical composition of defects in glass, for inclusions of residues from batch ingredients, or incomplete assimilation of "stones" from the refractory linings of tank furnaces. Here is a wide and important field for application of quantitative-analytical point-to-point controls of foreign elements introduced into the glass in critical, although minimum concentrations.[131]

[130] *Verres Refract.* **22**, (2), 45–162 (1968); *Silicates Ind.* **34**, (10), 269–275 (1969).

[131] See also examples from practical experience in the study of inclusions in glass; older literature see in Vol. II.B. ¶ 203 ff.).

Chapter II

Fining of Molten Glass

INTRODUCTION: BUBBLES IN GLASS AND THE NATURE OF THEIR GASEOUS CONTENTS

75. In a comprehensive report presented by M. Boffé, G. Pécriaux, and E. Plumat[1] the formation of gas bubbles is described in late stages of homogenization and fining, (cf. Vol. II.B. ¶ 30 ff., 43 ff.). This is a typical remelting side effect that we consider further in cf. ¶ 93, 98, but which we emphasize here as a recurrent phenomenon of the gas contents of the glass melt in those stages.

76. In their fundamental studies on the determination of diffusion coefficients of stable gases in glass melting, G. H. Frischat and H. J. Oel[2] described an ingenious method for multiple micrometric measurements of the decreasing diameter and ensuing shrinkage in volume of gas bubbles (filled with He) which had been artificially introduced into a complex Na – Ca – Mg silicate glass melt during the diffusion process. A mathematical approximation could be developed to illustrate the mechanism of the gas flow by mass transfer in the viscous liquid phase, for which the Hagen–Poiseuille and Knudsen equations are valid—and as a movement of the gas through structural cavities in the glass—as a hydrodynamic problem. The equations found satisfactory, illustrate the diffusion of 80% of the total bubble volume; in the residual 20% the influence of foreign accessorial gases, also of water, makes the diffusion anomalous even when the foreign ingredients make up only 3 to 5% of the total volume. Among the experimental results in the temperature range from 940° to 1250°C, we may pick out as illustrative paradigmata the shrinkage curves of four He bubbles, over a time period of 3000–4000 seconds (Fig. 17) (cf. Vol. IV.A. ¶ 11. Footnote 17, and Vol. IV. B. ¶ 40).

[1] Symp. on Nucleation and Crystallization during Devitrification and Remelting of Crystals in Glass, pp. 42–44. Amer. Ceram. Soc. Publ. Columbus, Ohio, 1962.

[2] *Glastech. Ber.* **38**, (4), 156–166 (1965).

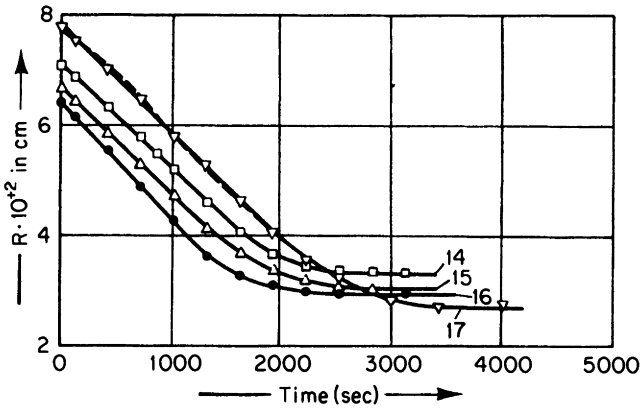


FIG. 17. Dissolution of four He-filled bubbles at 1170°C as a time function. (Frischat and Oel).

77. Frischat and Oel[3] used the elegant method of bubble shrinkage determinations for an intrinsic study of the gas diffusion reactions of He and Ne in glasses. There is an elementary correlation between the decrease in the bubble volume and the dissolution time of those rare gases when convection influences can be controlled; the diffusion builds up a gradient of gas concentration in the glass melt surrounding the viscosity which is a second factor in the convection and dissolution process. The essential factor in the experimentally observed effects is the shrinkage of the bubble sizes, measured telemicroscopically which indicates the systematic reduction of the volume of the rare gas linked to the diffusion process. The accurate calculation of these complex reactions can be mastered by the combination of a sphere movement model through an elementary viscous liquid (ruled by Stokes–Einstein law), with a movement of the rare gas atoms through channels or holes in the glass structure medium (application of the Kudsen laws). The choice of adequate combinations of both processes gave convincing support to experimental data, at temperatures between 900 and 1000°C, and provides a satisfactory model for noble gas diffusion in a commercial Na–Ca–Mg silicate glass, the melt of which had the disturbing contents of N_2, Co, Co_2, and other gas relics carefully removed.

78. Concerning the physical conditions of the origin of bubbles on contacts of refractories and glass in tank furnaces, K. H. Sandmeyer and W. A. Miller[4] were able to determine the potentials built up on the contacts also on phase boundaries between the gas and an oversaturated melt. The same problem, but seen more

[3] *Phys. Chem. Glasses* **8**, (3), 92–95 (1967); cf. Ch. H. Greene and I. Mitano, Vol. II.B. ¶ 39 ff.
[4] *Glass Ind.* **46**, (7), 410–411 (1965).

from phase boundaries of glass melt furnace atmosphere, discussed by K. H. Schier, W. Bauer, and R. Ehrig[5] appears for oxygen partial pressure potentials in reactions with the batch constituents, and is characterized in vertical cross sections of the liquid bath. The fact is to be considered that heterogeneous thermodynamic gas equilibria can never be attained in the industrial furnaces. Nevertheless, controlled observations of the action of fining additions like As_2O_3 or Sb_2O_3, could be made, combined with observation of the O_2 and CO_2 contents in the flame gases, and a systematic counting of the numbers of bubbles evolved in 100 cm^3 from the gas-chromatographic analytical data, using special methods developed by K. H. Schier, W. Bauer, and W. Müller.[6] At the beginning of the glass fining, the bubbles contained practically only O_2, but during the progressive fining N_2 was observed. The fining effect proved to become increasingly better the more that N_2 became the prevailing gas in the bubbles chemically dissolved, according to H. O. Mulfinger and M. Meyer.[7] When Sb_2O_3 was replaced by NaCl as the fining aid, the latter agent in its vapor phase was not able to form new bubble nuclei; it could only enter existing bubbles by diffusion, and enlarge the bubble sizes thus accelerating the glass fining melt by rising to the surface.

79. A rich source of information on the problems of gases in glass, including the kinetics of gas dissolution, was presented by G. J. Roberts[8]; J. F. Wosinski and J. R. Kearney[9] reported on the mass-spectrometric determination of the contents of glass bubbles and pin holes, combined with the chemical-analytical identification of the principal fining gases, after Dalton and Voss. This report is particularly interesting from the practical viewpoints because it is demonstrated that errors in the operation of fining, and more incidental contaminations by oil droplets, carbides, and the like could be detected. Not to be neglected must be electrochemical (galvanic) sources of oxygen bubbles, e.g., on the platinized protection tubes of thermocouples.

80. The fact that in most frequent observations of the glass fining operation, sulfates or nitrates of alkalies and alkaline earths are used which create gas bubbles in the batch reactions during the fining period, was studied by K. V. Nagulevich and Yu. I. Kolesov.[10] They include experience derived from the manufacture of glass fibers by remelting rods of special glass which, in this stage, show a pronounced tendency to evolve recidivistic bubbling. Alkali-free Al–B silicate glasses are of

[5] *Silikattechnik* **17**, (2), 41–43 (1966).
[6] *Silikattechnik* **16**, 158–159 (1965).
[7] *Glastech. Ber.* **36**, 481–483 (1963).
[8] Cf. Symp. "Gases in Glass," Sheffield, April 1966; *Glass Technol.* **7**, (6), 187–192 (1966).
[9] *Amer. Ceram. Soc. Bull.* **45**, (11), 1001–1003 (1966).
[10] *Steklo Keram.* **25**, (56), 344–347 (1968).

this type, which are fined with Ca and Ba nitrate and NH_4 salts. Under reduced pressures (440 mm Hg) the temperature range from 1140° to 1280°C is particularly critical, and a distinct individual "foaming temperature" is observed. On the other hand, addition of As_2O_3 counteracts such anomalies as recidivistic foaming.

For many details of solubility and diffusion phenomena of technologically important gases in glass melts, we refer to the excellent monographic article by L. Němec.[11]

81. The classical example of O_2- and SO_2-containing gas bubbles in fining glass melts was recently treated anew by C. H. Greene and D. R. Platts,[12] starting from a 2% Al_2O_3-containing Na–Ca silicate glass, fined with As_2O_3 and/or Fe_2O_3. All of the bubbles showed a shrinkage tendency by dissolution of the gas contents at 1170°C. A mixture of Na_2CO_3 and As_2O_3 specially increased the rate of shrinkage for O_2, whereas for SO_2 the corresponding effect was only subordinate. An indispensable condition of these solution effects for the gases in glass is the presence of one or the other element which has a variable chemical valence; this is the case with As. Na_2SO_4 alone has no effect on the shrinkage of the bubbles containing O_2 and SO_2. The course by which the bubbles undergo reaction and shrink follows a square root of time law rather closely, thus indicating that the rate determining mechanism is that of diffusion.

82. Interesting condensates of free sulfur and iodine in gas-filled bubbles in glass were studied by C. P. Fowkes and C. Parton.[13] Such bubbles are under vacuum at room temperature. The nature of the crystalline deposits could be determined simply by chemical methods and by the petrographic-microscopic identification which is commonly used for the disclosure of the nature of sublimates on the walls of inclusions in rock-forming volcanic ejectamenta, with the heating microscope stage. Instructive micrographs and a list of solid deposits and inclusions in fining glass bubbles were presented by P. Angenot.[14]

83. Confirming the previous observations of C. Kröger *et al.* (cf. ¶ 29, 38 ff.) on foam evolution on the surface of glass tank melts, P. Emer[15] could observe that in glass batches containing natural *phonolite* rock material as a substitute for quartz sand is an important source of an anomalously intense foam formation (boiling). The surface quality is also improved by the addition of fly ash. Emer speaks from

[11] *Silikáty* **13**, (4), 347–372 (1969) (cf. Vol. II.B. ¶ 80 ff., 86 ff.).

[12] *J. Amer. Ceram. Soc.* **52**, (2), 106–109 (1969).

[13] *Glass Technol.* **10**, (5), 147–150 (1969).

[14] Sympos, sur l'affinage du verre, Union Sci. Continental du Verre, Paris, 1955, pp. 107–120; "amorphous" and "crystalline" deposits were distinguished; see also W. and S. Kruszewski, *ibid.* pp. 223–232.

[15] *Glastech. Ber.* **42**, (6), 221–228 (1969).

extensive practical experience when underlining the sensitivity of the SO_2-SO_3 household in the boiling reactions, and demonstrates decomposition curves of sulfate-containing batches up to the high temperature of complete decomposition of Na_2SO_4 above 1400°C to explain the much delayed removal of the gases from the surface and the inner of the glass in the fining process. Typical sulfate foam may contain up to 0.8% SO_3. Particles of residual phonolite show the crystallization of leucite and nosean, surrounded by "nests" of gas bubbles amidst a glass of a relatively high viscosity and surface tension. In small-scale experiments additions of NaOH or NaSH to the fining glass may be recommended to accelerate the breakdown of sulfate in the foam formation.

84. Concerning the diffusion of He and Ne through silica glass (cf. ¶ 209), we emphasize the very distinct influences of *thermal history* of the glass wall material of the bubbles, on the rate of diffusion as observed, not for He, but so much more for Ne which was observed recently by K. P. Srivastava and G. J. Roberts.[16] Evidently, the larger atom radius of Ne in a comparison of both inert gases is the reason why the rate of diffusion, the diffusion coefficient, the activation energy, and the preexponential term are influenced by thermal history effects. Calculations make it evident that by using the pentagonal ring orifice size dimensions (Fig. 18) in the structure model for silica glass as proposed by L. W. Tilton[17] even slight variations of the atomic distance Si—O may be an important factor in those observed effects. It may be anticipated that all gases with an atomic (or molecular) size

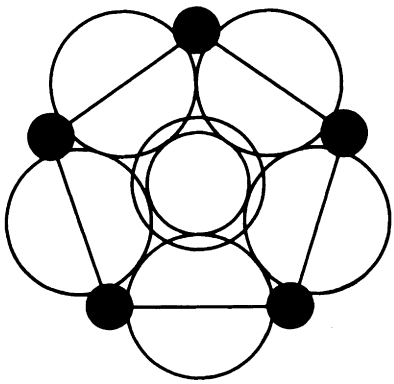


FIG. 18. Planar representation of a pentagonal ring with an Si—O—Si bond angle of 150°; orifice radius = 0.94 Å; size of a neon atom (r = 1.2 Å) is shown for comparison. (Srivastava and Roberts.)

[16] *Phys. Chem. Glasses* **11**, (2), 21–24 (1970).

[17] *J. Res. Nat. Bur. Stand.* **59**, (2), 137–154 (1957); on the "Vitron" theory cf. Vol. II.A. ¶ 209 f.

radius larger than that of Ne will for the same reason show the thermal history effect as mentioned above. L. C. Walters[18] discussed the same principles as factors ruling the permeability of borosilicate glasses for He and D as a consequence of the structural widths of glasses as a function of temperature, and of thermal history; equally, changes may be caused by different cooling rates (cf. Vol. IV.A. ¶ 11 ff., 19 ff.).

85. An extensive special report on the chemical processes of glass fining with specific features of the *resorption* mechanism by *retrograde reactions*, as are the *redissolution* phenomena of gases visible in the shrinking of gas bubbles (see ¶ 77, 81), was recently given by B. Dubaele[19]; also the additional influences exerted by combustion gases in the furnace atmosphere which causes manifold oxidation and reduction reactions noted in the degrees of activation of oxygen, the basicity of the alkalies, and the role of fining agents like As_2O_3 were repeated.

86. As an interesting supplement to the studies of the gas contents of fining bubbles, we may add observations made by P. R. Wengert and M. Bayard[20] on *crystalline* phases which were identified as inclusions in bubbles and could be isolated and subjected to phase analysis under the optical microscope, the electron microscope, and the electron-beam microprobe to X-ray diffraction, or by special methods like gas chromatography (¶ 58, 78) and mass spectrometry (cf. ¶ 59 ff., 79). Of the numerous examples demonstrated by Wengert and Bayard, we may enumerate the oxides and sulfides of Fe, Cu, As, the sulfates, sulfites, and sulfides of Na, as well as elements like Si, I, Ni, Fe, Cu, and in special glasses, $PbTiO_3$. Whereas for such crystallites in bubbles of more than 0.5 mm in diameter, the hot-stage microscope method of M. Fowkes and C. Parton (cf. ¶ 82) is more convenient, real microcrystallites are better isolated from smaller bubbles in a fluid plastic, and transferred into a suitable substrate to protect the samples from any changes by hydration or other atmospheric conditions.

87. Kl. P. Hanke and H. Scholze[21] recently studied the influence of water vapor on the bubble evolution in sulfate-containing glass melts. When water vapor is conducted over such glass melts, quite definite temperatures are observed above which bubbling sets in. The higher the H_2O partial pressure, and the SO_3 content of the glass, the lower are these characteristic temperatures. When the glass melt is saturated with steam under a constant water partial pressure, every sulfate anion in the melt is exchanged by 4 OH^- ions. The bubble evolution, as

[18] *J. Amer. Ceram. Soc.* **53**, (5), 188–189 (1970).
[19] *Verres Refract.* **24**, (3), 141–145 (1970).
[20] *Amer. Ceram. Soc. Bull.* **50**, (12), 976–981 (1971).
[21] *Glastech. Ber.* **43**, (12), 475–482 (1970).

such, is caused by an accelerated water vapor evolution and follows a heterogeneous gas reaction of the type

$$SO_4^{2-} + 3 \rightarrow Si-O-Si \leftarrow + 2\,H_2O \rightleftharpoons SO_3 + \rightarrow Si-OH + 2 \rightarrow Si-O^-$$

combined with water vapor evolution as a heterogeneous reaction of the type $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$. The higher the partial pressure of oxygen, the more the equilibrium is shifted and the rate of increasing SO_2 concentration reduced. These latter reactions indicate practical possibilities to avoid any bubble evolution under quite distinct experimental conditions. Since a high residual SO_3 content promotes tendencies to form secondary bubbles (reboiling), it is recommended that the SO_3 content be kept as low as possible, at least to damp it to a tolerable minimum. For the latter possibility it may be feasible to raise the H_2O partial pressure suddenly by an intense bubbling with steam. This shockwise increase application may essentially promote the fining.

PRACTICAL FINING EXPERIENCE. DETAILS OF FINING TECHNIQUES

88. Typical examples of a normal Na_2SO_4 fining operation for industrial glass melts are described by M. M. Bhuyian and M. Cable.[22] The comparison of two somewhat different Na–Ca silicate glasses in their fining characteristics with Na-sulfate (SO_3 content 0.3 wt%), at 1400° and 1475°C, showed differences which were assumed to be due to different oxygen partial pressures in the furnace gas atmosphere, and differences in the temperatures applied to the glass melts. As an indicator of striking variations in P_{O_2} an addition of 0.1% Cr_2O_3 was used, as well as the observation of shifts in the intensities of the 655–mμ absorption band. The two experimental glasses showed increasing P_{O_2} with increasing temperature, but at different rates. Additions of Sb_2O_3 or As_2O_3 acted as weakly reducing, but addition of Na_2O_2 increased the concentration in Cr^{3+} ions. Both oxides promoted the fining effects. Under the action of SO_3 as the fining agent, the number of fining bubbles was actually reduced when the SO_3 contents were increased from 0.3 to 0.4%.[23] We expressively repeat our reference to the investigations reported by G. J. Roberts in several outstanding contributions of different authors to a Symposium on Gases

[22] *Glass Technol.* **6**, (6), 206–212 (1965).

[23] Cf. A. K. Lyle, Trav. Congr. Int. du Verre, 4th, Paris, 1956, Rep. 94–102; his previous results were confirmed by Bhuyian and Cable's more recent data; one may also compare the latter glass melt experiments with those of F. Ya. Kharitonov and L. G. Mel'nichenko (*Steklo Keram.* **22**, (9/10), 611–616 (1965); cf. ¶ 27, footnote 39, in their experiments with SO_3 additions of 0.6%.

in Glass. To these we rubricate the later publication of M. Cable[24] on the kinetics and mechanisms of fining, and his hypotheses, for a deeper understanding. Also important in this correlation is a publication on the spontaneous evolution of gas bubbles in melts of simple binary alkali silicate compositions when the batches containing Na_2SO_4 and the atmosphere above the melts were under variable oxygen partial pressures, as discussed by C. G. Rasul and M. Cable.[25]

89. Concerning the instrumentation for accurate observations of fining processes, M. Prod'homme[26] explicitly discussed the principles of light scattering (according to Lord Rayleigh's and R. Gans theoretical treatment of these phenomena, cf. Vol. VII. ¶ 515 f.) in all problems of phase unmixing and the discrimination in glass technology. A. Winter[27] used specialized optical methods for accurate measurements during the fining process, following the viewpoints of tyndallometry and turbidimetric methods, specifically L. Prod'homme's visual diffusiometer[28] by the elementary determinations of the ratio $\dot{I}_{90}/\dot{I}_0$ ($\dot{I}_0$ is the intensity of the incident light, $\dot{I}_{90}$ the light intensity observed under an incidence angle of 90° to this direction). Bubbles reflecting the incident light are indicated by sharp signals in the diffusiometer. Bubbles of equal diameter may sometimes behave differently, when caused by varying gas pressure conditions in the fillings. There may occur either an enrichment near the bubbles or a local impoverishment in the gas by absorption into the bubbles. Local increases in the intensity of the diffused light may indicate a gas enrichment before the bubbles were formed. Diffusiometry is, therefore, a sensitive method for the control of the normal development of the fining process for optical glass, and related important special tests.[29]

90. It is fascinating to pursue in the glass technological literature, steadily increasing endeavors for a rationalization of the glass production processes. In the historical development from the classical pot furnace to the modern tank furnace, not only the desire for increased mass production and improved heat economy of the process was the driving force; most evident were deeper needs for better knowledge of the fundamentally important batch reactions and the control of the fining processes. Witnesses of this tendency are the many highly specialized and ingenious inventions and proposals for the construction of more efficient glass melting furnaces and machines. We recommend as a really up-to-date report from this point of view the

[24] *J. Amer. Ceram. Soc.* **49**, (4), 436–441 (1966), with important bibliography.

[25] *J. Amer. Ceram. Soc.* **49**, (10), 568–571 (1966).

[26] *Rev. Opt. Theor. Instrum.* **45**, (4), 163–166 (1966).

[27] *Verres Refract.* **21**, (3), 141–145 (1967).

[28] Cf. *Rev. Opt. Theor. Instrum.* **32**, 615 (1953).

[29] See also A. Winter, *Verres Refract.* **21**, (6), 509–513 (1967); and a communication in the Symp. on Defects in Glass, Tokyo and Kyoto, 1966, No. 9, pp. 87–107.

comprehensive and excellently illustrated article by E. Plumat, P. Éloy, J. Duthoit, and J. U. Barbier[30] from which it is seen to what an impressive degree the fundamental ideas for improvement of intensity and acceleration of the batch fusion and the fining have been achieved.

91. For the production of amber-colored glass products, it is generally known that the application of *blast furnace slags* in the raw batch composition is particularly suitable because of its content in the *sulfides* of Ca and Mn (cf. Vol. II.C. ¶ 47). But the slags, beyond that, act definitely favorably in promoting the fining processes as it was demonstrated by R. Persson[31] from the practical points of view. The contamination of the slag by metallic Fe can, of course, be easily separated from the silicate substance by a magnet grader; the slag substance accelerates the fining process and promotes the elimination of gas bubbles, which is not, in the same measure, the case with feldspar or similar ingredients of the batch mixture. Studies made with the differential-thermal analysis method made it evident that the endothermic reaction range, which for normal batch mixtures containing feldspar and the like, starts at 710°C, begins in a batch containing blast furnace slag at about 640°C, in good agreement between laboratory and practical experience. At the same time, the efficiency of the fusion furnace is increased by about 20%.

92. A study of the fining process as promoted by an *addition of sodium sulfate* to the batch for container glass was presented by F. Shaw and S. P. Jones[32] after observations in an electrically heated laboratory furnace. For an amount of 1000 wt parts of quartz sand, the sulfate addition was chosen to be 0, 2.5, 5.5, 7.5, 10.0 wt parts of sulfate; the furnace atmosphere was varied: normal air, nitrogen, pure nitrogen + SO_2, air + SO_2, nitrogen + SO_2, nitrogen + CO. The results of the experiments make it evident that additions of less than 5 parts Na_2SO_4 have no positive effect on the fining process; sometimes even the contrary could be observed. More than 5 parts (significantly for 7.5 parts of Na_2SO_4) caused a distinctly positive effect on the fining reactions. When the furnace atmosphere contained SO_2 the improvement effect was particularly significant.

93. "Reboil" effects in glass were critically discussed by F. D. Lorey[33] in the meaning of a sudden release of large gas quantities which can be "triggered" by a severe change in temperature or by mechanical agitation. Lorey, however, demonstrated that the reboiling phenomena may have other different sources, many of which are somewhat hidden, and require deeper basic studies than actually are available. The results to be expected must start from the physical and chemical

[30] *Glastech. Ber.* **40**, (11), 411–425 (1967).
[31] *Glass Ind.* **47**, (10), 537–539 (1966), 583–584.
[32] *Bull. Amer. Ceram. Soc.* **45**, (11), 1004–1008 (1966).
[33] *Bull. Amer. Ceram. Soc.* **45**, (11), 1012–1013 (1966).

conditions ruling, like changes in temperature and pressure, related to the thermal history of the system in question, including also defects in how the fining operation was conducted, like poor mixing in the batch, or the influence of dissolved refractory lining material in the glass, or volatilization of alkalies, and changes in the chemical characteristics of the furnace atmosphere, not to omit electrochemical sources of anomalous potentials.

94. L. Šašek[34] investigated the effects of small additions of NaCl to glass batches, by differential-thermal analysis, thermogravimetric analysis, and electrical conductivity. The liquefaction is indicated by the fusion of the $NaCl-Na_2CO_3$ eutectic (at 615°C) which distinctly promotes the dissolution of silica at relatively low temperatures. The higher the temperature the greater the influence exerted by a volatilization of NaCl, and an undesirable flotation effect will transport the sand grains of the batch to the surface of the glass melt. A simultaneous addition of Na_2SO_4 to the batch, however, can dampen this process to a high degree. An optimum for this correction and intensification of the batch reaction was achieved by the addition of 0.33 wt % NaCl and Na_2SO_4.

95. Effects of fluorine and chlorine anions in batches and fining melts of Na – Ca and K – Ba silicate glasses in their effects on the rate of reactions of fining process and degree, viscosity, and surface tension of the resulting melts, were observed by C. Hirayama and F. E. Camp.[35] The viscosity of the glass is significantly reduced by the action of F^- anions, but increased by Cl^-. Probably this latter effect for Cl^- is coupled with high alkali losses by volatilization of NaCl and KF from the surface of the melts at temperatures between 1250° and 1400°C. The F^- ions are much better retained (50–75% are estimated) in cooperation with the effects of simultaneous additions of Sb_2O_3 or As_2O_3 as fining agents. For metallurgical slag melts (cf. Vol. II.C. ¶ 39) quite analogous effects of the halogen ions are observed, and the application of fluorite (CaF_2) as a fluxing agent is of high technological significance.

96. The electric conductivity of batches for Na – Ca silicate glass during all the characteristic states of the fusion and fining processes was extensively studied by C. Kröger and H. Beckmann[36] (cf. Vol. II.A. ¶ 147), for an experimental mixture of 1 mole Na_2CO_3, 1 mole $CaCO_3$ (as limestone), and 4.8 moles SiO_2 (as quartz sand). The conductance vs time and temperature curves are highly suitable for continuous control of the reactions, particularly also for a correction with borax, Sb_2O_3, and the like, as fining agents. The curves show (a) a typical degassing period and (b) a homogenization period, the latter reaching a maximum conductance after the period

[34] *Collected Paps. Chem.-Technol. Inst. Prague, Ser. Inorgan, Chem. Technol.* **29**, 183–200 (1966).
[35] *Glass Technol.* **10**, (5), 123–127 (1969).
[36] *Glastech. Ber.* **40**, (4), 121–124 (1967).

(a) is finished. When limestone is replaced by dolomite, the fining period will be somewhat shortened, particularly when typical fining agents are added. A distinct decrease in conductance in the later portions of the curves can be explained by the development of larger aggregation complexes in the frameworks of the silicates formed by "inner friction" and a decrease in mobility of the alkali ions.

97. D. Tentulescu, I. Wagner, and I. Fichman[37] used Roumanian alabaster to replace Na_2SO_4 as a fining agent for industrial glass. A well-known impediment for this interesting modification of the commonly used practice is the fact that gypsum (the mineral substance of alabaster) shows early high losses in SO_3 from the glass batch, but this might be compensated to a certain degree by additions of reducing agents (like carbon) at a working temperature of 1350°C.

98. In soda–lime silicate glass melts, M. Cable, C. G. Rasul, and J. Savage[38] observed a repetition of the foaming phenomenon and reboiling when the finished glass was reheated in a controlled gas atmosphere. Typical foaming, however, occurs only with sulfate-containing melts, and exclusively in oxidizing atmospheres. Particularly striking and reproducible is the foaming in dry oxygen, but the evolution of foam is easier running in moist O_2. In every case, foaming indicates considerable loss in SO_3 for the melt. So-called "reboil seeds" are formed after fining when a glass melt (Na – Ca silicate glass) is cooled from 1400° to 1100°C, particularly in dry pure oxygen. A certain difference from reboiling phenomena may be seen in foam bubbles of the type discussed here, formed near the melt surface. They react very quickly to changes in the surrounding gas atmospheres, whereas reboil bubbles are formed distinctly in deeper zones of the melt and respond to changes in the atmosphere much more slowly. In general, reboiling involves the evolution of much smaller gas amounts than foaming, does not require the presence of a gas of high solubility (SO_3) and does not evolve in foam-stabilizing mechanisms. Melts containing SO_3 could be made reboiling in nitrogen atmospheres.

99. For a comprehension of experimental and practical experience of glass fining, with agents like Na_2SO_4 or As_2O_3, we may now present an essential reference to a very recent publication by R. Kenworthy[39] on normal glass batches containing some free carbon (introduced mostly as anthracite), to create a reducing atmosphere and a rapid formation of the highly reactive CaS, to melt Na_2Co_3 [or $Na_2Ca(CO_3)_2$].[40] By observation in the hot-stage microscope, Kenworthy described in detail how sluggish such batch reactions are when additions of Na_2SO_4 were lacking, specifically

[37] *Proc. Conf.* Silicate Industry (SILICONF), 9th, Budapest, 1967 (1968), pp. 515–518.

[38] *Glass Technol.* **9**, (2), 25–31 (1968).

[39] *Silicates Ind.* **37**, (10), 245–257 (1972).

[40] See also M. M. Bhuiyan and M. Cable, ¶ 88; furthermore A. R. Conroy, W. H. Manring, and W. C. Bauer, *Glass Ind.* **46**, (2), 84–89 (1966); **46**, 133–139 (1966).

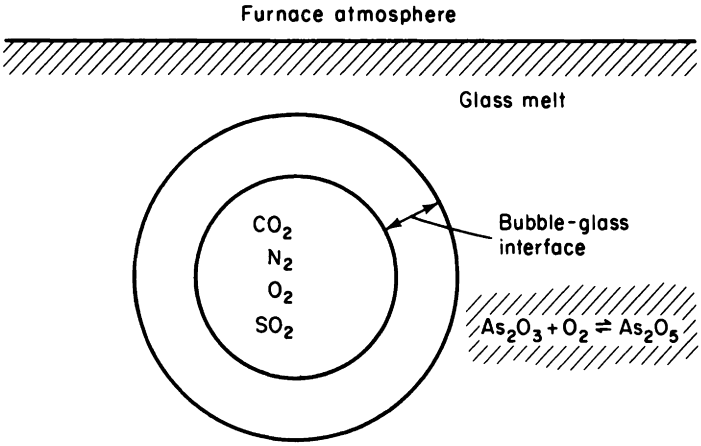


FIG. 19. Schematic section through a gas bubble in glass melt. (Kenworthy.)

the dissolution of limestone and the sand grains, and how promptly the conversion to a Na–Ca silicate glass takes place when the molten Na sulfate acts like a "lubricant" in the partially unmixing melt phases, accelerating the gas evolution and the bubbling from the batch, rising to the glass melt surface under the action of surface energy effects (see Fig. 19), and maintaining a rapid diffusion current and intense convection (cf. R. Brückner).[41]

100. Kenworthy focused his attention particularly onto the conditions of a rapid fining process, and used for a quantitative study the "seediness" of the resulting glass, calling N the number of gas seeds counted per cm^3 in the samples of foaming glass. He extended his observations in the next step onto the introduction of non-sulfate fining agents like As_2O_3, $NaNO_3$, Na_2O_2, with N as a function of time (cf. Ch. H. Greene, ¶ 81), namely, as a function of $\sqrt{t}$ to fulfill the characteristic of the fining process as a typical diffusion reaction. As_2O_3 acts in this respect in a double way, namely, (1) by absorption of oxygen from the gas bubbles, and (2) to control the oxygen activity in the glass melts, i.e., indirectly the solubility of SO_3. In connection with this action of As_2O_3, Kenworthy (in this special point following Brückner) sees as the essential factor in fining, the "disruption" effects through interfacial layers in the glass melt/bubble phase systems of the later stages on fusion and fining, increasing the mass transfer across interfaces, the relative amounts reacting as a function of the depth distance from the interface glass melt/atmosphere in which the SO_3 concentration is high, but Na_2O impoverished, to restore equi-

[41] Cf. R. Brückner, *Glastech. Ber.* **34**, (9), 438–456 (1961); **34**, (11), 515–528 (1961); **35**, (2), 93–105 (1962).

librium conditions. As_2O_3 chiefly acts as an oxygen "remover" by reducing reactions in the temperature range from 700° to 1200°C. The inverse reaction takes place, releasing oxygen into the glass melt, and showing a tendency to enrich the surface of the glass melt in SO_3 by oxidation of SO_2 involved in the previous reaction steps.

101. Secondary bubble generation in melts for carbon-amber glass was described and experimentally reproduced under simulating conditions (at 1250°C and controlled stirring) by P. Emer.[42] In the experiments, the foaming occurs surprisingly abruptly, particularly when the batch is melted *in vacuo* (H_2O is subordinate in the gas content of the bubbles, CO_2 and SO_2 being predominant). For the industrial production of coal-amber glass, it is essential that the batch contains a relatively fine-grained quartz sand (with grains of 0.1 to 0.2 mm in size) and that fluxing agents (like NaCl, borax, fluorite as accelerators) be added. The latter very markedly reduce the intensity of reboilings when coal–amber glass is to be prepared for commercial use.

HYDRODYNAMIC FLOW CONDITIONS IN THE GLASS BATH

102. The paramount factors ruling the basic importance of homogenization and fining conditions in the glass bath received much attention in technical research in recent years. Particularly the electrical conductivity of molten glass offers many fundamental possibilities for control and improvement of self-homogenization by a cycling flow phenomenon which previously had been studied exclusively by a careful observation of the local distribution of striae heterogeneities in single sections and calculation of the apparent diffusion constant of indicator cations like Ca^{2+} or Zn^{2+} to make backward conclusions for a more or less satisfactory rate of homogenization, namely by convection currents (H. Shimada, 1952; cf. Vol. II.B. ¶43). It was a remarkable new advancement when V. A. Dubrovskiĭ (1957) demonstrated the usefulness of Sr^{2+} distribution, when this cation was doped and activated in the radioactive tracer isotope Sr^{89} for such studies. This elegant and highly sensitive method which was improved in important details by later investigations, is the most important step forward to a sufficiently refined general scheme for the current regulation of the homogenization process in normal tank furnaces.

103. J. Staněk, L. Šašek, and H. Meissnerova[43] first studied the temperature function of resistance (and conductance) of the molten glass as the basis for all details of flow conduction up to 1550°C, using a frequency of alternating current

[42] *Glastech. Ber.* **37**, (2), 59–69 (1964).

[43] Proc. Conf. Silicate Industry (SILICONF), 8th, Budapest, 1965 (1966), pp. 557–578, specifically pp. 569–578 on "model" conditions for experiments in electric heated glass furnaces.

of 800 cycles/second to avoid polarization, and applying potentiometer-oscilloscope measurements. The resistivity of low-alkaline and Pb silicate glasses increases very rapidly with decreasing temperature, and the slope of the resulting curves is of particular importance for a correct adjustment of the electric melting process to rule conductance in hotter and cooler portions of the glass bath and to overcome badly disturbing deregulating effects (E. Borel, 1950). Graphite electrodes first were used but molybdenum electrodes have replaced them in glass melting units of the type developed by Borel in which the electrodes must be fixed near the glass surface (25 to 50 mm below it) to create a strong ascending heat convection and an intense stirring effect. Omitting in our text details of other special furnace constructions (e.g., after P. A. M. Gell, 1956; and L. Penberthy, 1959), we recommend in Staněk *et al.* a careful study of the basic calculation for "modeling" an "ideal" electric melting furnace, with heat-transfer conditions and convection parameters, by application of the Fourier–Kirchhoff differential equations, and the viscous flow in the glass bath (by following the Navier–Stokes equation). Such calculations permit a comparison of models of defined kinematic viscosity from carefully chosen liquid-phase model substances (preferably glycerol), with the conditions for glass flow.

104. An excellent introductory report on real glass flow data in tank furnaces and the conditions observed in industrial plant units, may be indicated in the article by G. Steinke,[44] with its helpful literature references and illustrations which orient on the performance of measurements of temperature and distribution data, and the principles for using radioactive tracer methods. The kinematic conditions for a cycling flow phenomenon in large tank units are also indicated in brief descriptions and diagrams, but Steinke's are specifically valuable for an understanding of the pending research problems in view of practical requirements for the steady control of flow conditions in medium-sized container glass furnaces, and cross-fired tanks. On the other hand, A. R. Cooper[45] discussed the kinematics of *mixing* in continuous glass baths, and the local mixing rates in laminar flow, as expressed in the ratio $D/\delta^2 U_x$ (with D = the chemical diffusion constant, δ the striation thickness, U_x the "throughout velocity," for a simplification of the calculation from three-dimensional models). For $dln/dt = -dU_1/dt$, the time function of the incremental length l and the velocity component in the striation direction can be determined. This includes also the shear conditions, the reduction of the cross-sectional area, and rotation effects, as shown in diagrams like Fig. 20, which rule the thickness of the various oriented striations and their attenuation, e.g., for a parabolic distribution of the

[44] *Sprechsaal* **99**, (9), 323–339 (1966).
[45] *Glass Technol.* **7**, (1), 2–11 (1966).

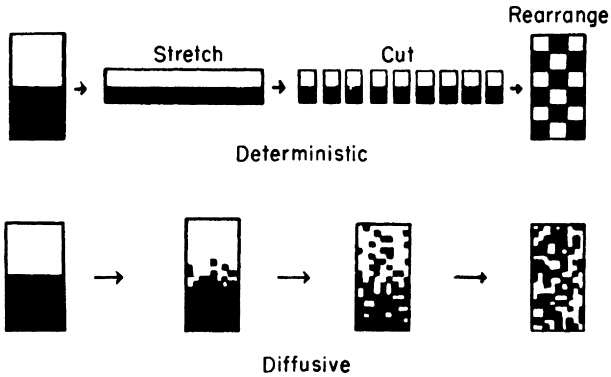


FIG. 20. Schematic diagrams showing the essential difference between deterministic and diffuse mixing. (Cooper.)

velocities (Fig. 21) or the reduction of cross-sectional area ($W/W_0 = \frac{1}{2}$). We omit here a discussion of the exterior, but practically very important and diversified origin of heterogeneities in glass melts, like volatilization losses, assimilation effects by dissolution refractory lining material, and the like. Cooper's theoretical discussions sufficiently illustrate the importance also of the chemical diffusion constant, what he called a "deterministic" mixing which reduces the heterogeneities by a successive attenuation (see the schematic Fig. 22), whereas in "diffusive" mixing the heterogeneities are diminished through the random motion of particles of all species.

105. The radioactive tracer method was used by P. Ksiazek and T. Najbar[46] (cf.

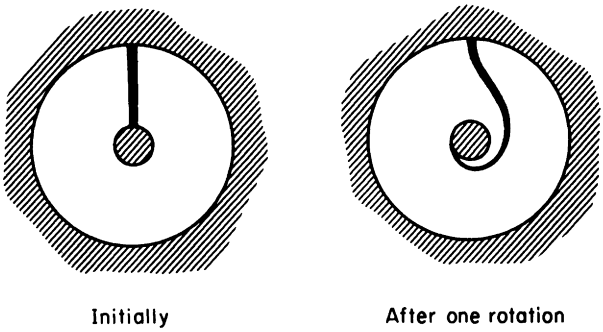


FIG. 21. Schematic diagram showing attenuation of radially oriented striae by one rotation of inner cylinder. (Cooper.)

[46] *Szkło Ceram.* **18**, (7), 202–205 (1967).

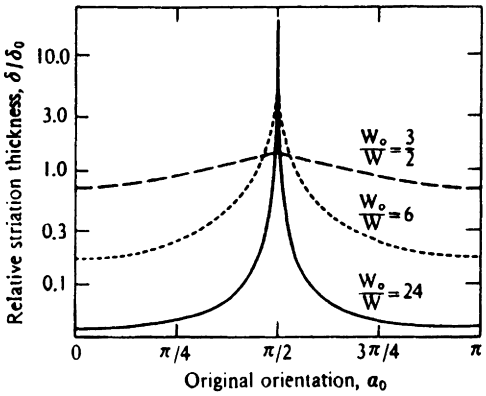


FIG. 22. Dependence of relative striation thickness on original orientation for several values of cross-sectional area reduction. (Cooper.)

¶ 180) for the general control of flow in the glass bath in tank furnaces (for plate glass) using the isotope Na^{24}. The results demonstrate a strong functional correlation of the general patterns of flow distribution in the glass, and the resulting quality of the glass product (plate glass). Under similar furnace conditions, J. Kelly[47] determined after doping with P^{32} or Nd^{147} (both are typical β-radiation emmitent) the radiation intensity as a function of time, and at the spot of the individual samplings, under both conditions of static and dynamic tank operation during the holding period of the glass in the tank reservoir. These data were compared with the results of the glycerol model experiments (in the dimensional ratio 1:50, the time ratio of 1:7) at 25°–100°C, corresponding to the viscosity ranges of the liquid glass from 1000°–1500°C, and including anomalies like skimming and irregularities in the schedule of throughput. For every single section of the furnace the transfer equations were controlled and adapted by analog computerization.

106. The particular advantage of radioactive tracer methods by *secondary activation* (i.e., irradiation with rapid neutrons of initially inactive tracer doped into finished glass samples), over the commonly used *direct* method (i.e., when the already radioactive tracer, as such, is introduced into the glass into the batch, usually at the beginning of glass production) was demonstrated by C. Bondy, J. P. Vidal, and G. Robin[48] (cf. ¶ 179). The two methods supplement each other[49] in such glass flow studies, for which the high sensitivity of the activation method is essential (for certain elements the intensity of the radiation limited from only 10^{-11} g of the

[47] *Verres Refract.* **19**, (1), 3–12 (1965).
[48] *Verres Refract.* **21**, (6), 524–529 (1967).
[49] Cf. B. Grislain, *Verres Refract.* **21**, (6), 514–523 (1967).

activated tracer is sufficient), e.g., for determinations of the absolute age of glass samples from different portions of the glass tank. R. Grislain recommends Ta^{182} as an element of great convenience for such purposes; no reduction in intensity of the signals and countings could be observed in sooner than three weeks, whereas for the so often used Na^{24} those decay phenomena are highly disturbing. The authors (Bondy, Vidal, and Robin) emphasize that in using the activation method, however, dummy experiments to detect the presence of contaminations in the activation program are indispensable. Besides Ta, rare-earth elements also may be highly suitable for measurements of the kind in question here for glass technological aims.

107. Grislain also reported on experiments made with P^{32} which was introduced over a melt solution in a glass with 51% P_2O_5, 34% K_2O, and 15% Al_2O_3, into window glass, to follow a strict distribution plan over the tank as such, the bridge wall portions, and eight drawing machine cells, in a fully automatic, computer-controlled and corrected program. The activity curves resulting from different sites show a sharp peak as soon as activated glass arrives in the flow, i.e., the spot of the distribution plan, and the ensuing continuous decay in intensity. The evaluation of such curves delivers the complete plan of the glass flow, indicating pronounced lateral shiftings in the concentration fronts and the well-known "hot spot" phenomenon, helicoidal movements parallel to the walls of the tank, and the typical asymmetries of the entire flow pattern (Fig. 23). Minor indications are for returns in periodic sequences, or suction effects in the vicinity of the drawing machines, and the like. The activation method for Ta^{182} is specifically suitable for the study of such effects in the operation vicinity of the working compartments.

108. O. Zych, E. Pejtek, and G. Štepán[50] (cf. ¶ 181) report on practical experiments using again the Na^{24} tracer method in glass tank furnaces in which the radioactivity was measured from spot to spot, with intensities varying from 0.5 up to 600 mC, when the doping was made on the glass surface, or immediately below it. The flows were currently tested by scintillation counters, through the lining of the tank, from case to case, and on samples drawn directly from the bulk melt. Highly complex flow conditions were observed in the drawing chambers, e.g., for the drawing of thick-walled glass tubes, with mutual overlappings of different patterns of variable rates of flowing, and even often undergoing back flow. Of great technological importance are determinations of glass transfer starting from the batch pile, to the tank neck, and the times required from section to section in the surface portions, as well as the back-flow phenomena, not only for normal tank furnaces but also for those electrically heated.

109. Rather similar results were achieved by J. Gemesi and J. Szöllösi[51] who

[50] *Silikaty* **13**, (1), 67–73 (1969).

[51] Proc. Conf. Silicate Industry (SILICONF), Budapest, 9th, 1967 (1968), pp. 467–477.

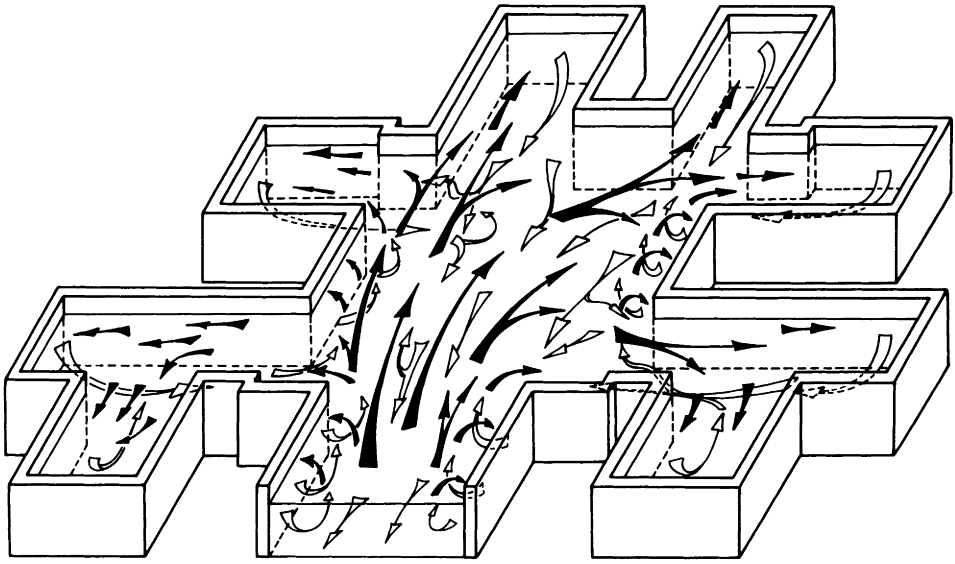


FIG. 23. Schematic overall sketch of flow patterns for the glass melt in a Pittsburgh-type fusion furnace. (Grislain.)

applied Na^{24} or Cr^{51} isotope tracers to get impressive curves showing back flows at feeders, near burners, surface flow near cleaning pockets, radioactivity distribution in different depths of the batch, and others. We also mention in the same connection a report by P. Ksiazek, T. Najbar, J. Byszewski, and M. Sura,[52] in tanks for different glass types, including, e.g., Pb crystal glass. Those authors normally worked with Na^{24} but in special cases, with Ca^{45}, Sc^{46}, Sr^{89}. Worth mentioning here is the nearly exclusive occurrence of asymmetric flow patterns of the type shown in the course of the furnace campaign. Characteristic is the helical-type flow current directed towards the working chambers. Dislocation of the "hot spot" can be observed when cold air anomalously comes into contact with the glass mirror.

110. *Cinematographic image analysis* was applied by D. D. Billings and W. H. Manring[53] (cf. ¶ 181) for studies of dislocations in melting down of the batch pile which may be seriously affected by low-licking flames causing *inversion of flow direction* from the normal course and thus change the hot-spot activity, particularly observed in high-production horseshoe (U-) flame tanks.

111. The flow phenomena in electric-heated glass furnaces were again described

[52] *Silikattechnik* **18**, (11), 345–349 (1967).
[53] *Glass Ind.* **50**, (8), 382–386 (1969).

in a more recent publication by J. Staněk, L. Šašek, and H. Meissnerová[54] (cf. ¶ 177). For this purpose, they considered model systems with glycerol (to which some LiCl had been added); those authors emphasize that it is not sufficient that analogies of models with tank conditions concern the physical parameters of viscosity and temperature, but that full analogy must also extend to conductance as a function of temperature. The often observed influence of shape factors chosen for one- or three-phase ac electrodes (shaped as plates or rods) on the development of flow patterns in the glass bath offer the possibility of controlling optimum conditions for the regime in the fusion zone of electric tank furnaces, when empirically the best-suited shape for the electrodes and their best position in the tank could be developed. It is essential for the success in this case to build up thermal barriers in the fusion zone. Experimental studies of different shapes of the electrodes and their position in relation with the lining walls of the tank revealed not only the optimum flow paths in the liquid glass bath but also conditions which, because of a comparatively high speed of flow, considerably increased corrosion of the refractory lining walls, as a most undesirable secondary event.

112. The *specific role of arsenic oxide as a fining agent of colored* glass may be discussed here first from the aspects of undesirable yellowish color tints of borosilicate glasses that frequently are developed even after the fining, under the action of traces of reducing carbon from contaminated sands. For these phenomena, P. Wange, H.-J.Blankenburg, and K. H. Jagusch[55] gave a detailed description[56] (cf. ¶ 208). The so-called "coal-yellow" or "amber" tint is *not* caused by colloid-dispersed carbon but by the presence of alkali sulfides and polysulfides, also sulfoferrites, i.e., the strongly staining anion on FeS_2^-. The yellow color of such glasses shows a strong absorption band at 400 to 430 mμ, and in the near ultraviolet between 300 to 400 mμ. Addition of As_2O_3 mixed with $NaNO_3$ is, in many cases, sufficient for a good fining and corrects the staining; addition of ZnO to the glass composition also has been recommended with success for this purpose.

113. A rapid, accurate, and fully reproducible analytical method for the estimation of the *redox conditions* in Fe- and S-containing amber glasses was recently developed by M. S. Zaman and A. Paul[57] (cf. ¶ 208, 280) based on the determination of the maximum optical density in the near infrared ($\lambda = 1\ \mu$) for Fe^{2+}, and that of sulfide anion and Fe by ICl, thus eliminating any side reactions in an aqueous solution

[54] *Glass Technol.* **10**, (2), 43–49 (1969).

[55] *Silikattechnik* **18**, (9), 282–285 (1967).

[56] On Hohenbocka sands containing humus substance, see e.g. H. J. Blankenburg, *Z. Angew. Geol.* **12**, 113–115 (1966).

[57] *Glass Technol.* **10**, (4), 93–98 (1969).

phase. Thereafter, the total Fe is best determined by reaction with thioglycolic acid, and a special method for total S.

114. Ch. H. Greene and H. A. Lee[58] studied the fining action of As_2O_3 (with small additions of $NaNO_3$), and the volume changes of bubbles (seeds) evolved in the glass melt when fined at 1100° to 1300°C, over a longer time period of suspension of the bubbles in the liquid phase. A square root of time function was derived from the experimental determination of volume changes of the bubbles decreasing in the measure as As_2O_3 was added, as a consequence of absorption of O_2 (see observations by M. Cable *et al.*, cf. ¶ 81, 88, 98). In the same way, resorption of O_2 in the melt is increased in speed as more As_2O_3 was introduced. The gas absorption is also influenced by the composition of the gas atmosphere of the fusion furnace units, and is different for gas-fired kilns and electrically heated systems. In the temperature range from 1065° to 1280°C the absorption increases; older observations made by Ch.H. Greene and I. Kitano[59] are revised and corrected in detail.

115. The effects of As_2O_3 in fining of sulfate-containing glass melts were studied by Y. Kokubu, J. Chiba, and Ts. Okamura[60] when 12% of the total Na_2O (for a normal Na–Ca–Mg silicate glass) was supplied as Na_2SO_4 (+ 3% carbon), molten in Pt–Au crucibles at 1400° and 1450°C. The seeds evolved were counted, their gas composition was determined by classical absorption methods. In these serial experiments the changes in the ratios of As in the trivalent and pentavalent states were important under variant melting conditions. The general result of the analytical data and their evaluation made it clear that As_2O_3 reduces the sulfate in the glass melt in the early range of glass fusion. The number of seeds spontaneously formed was counted; the principal gas contents of the bubbles was then SO_2. This means that oxidation prevails below 800°C. Above 1000°C, however, O_2 evolution from As_2O_5 prevails. On the other hand, As_2O_3 accelerates the dissolution of SO_2 in the glass bath.

116. In principle, a very similar series of problems was investigated by M. Cable, A. R. Clarke, and M. A. Haroon,[61] also for a typical common Na–Ca silicate glass composition, molten at 1400°C, with additions of 0.02 to 1.00 As_2O_3, and of $NaNO_3$ (to supply 0, 1, and 5% Na_2O in the glass composition). The gas composition was controlled by gas chromatography. When no As_2O_3 was added, the gases from the fining seeds were simply CO_2 to which increasing amounts of O_2 came when As_2O_3 had been introduced into the melt, under reaction with $NaNO_3$. A best grade of

[58] *J. Amer. Ceram. Soc.* **48**, (10), 528–533 (1965).

[59] *Glastech. Ber.* 32. K. Fifth Int. Congr. of Glass, 1959, Rep. Nos. V.44–V.48.

[60] *Asahi Garasu Kenkyu Hokoku* **16**, (1), 1–12 (1966).

[61] *Glass Technol.* **10**, (1), 15–21 (1969); **11**, (2), 48–53 (1970).

fining was observed when the O_2 content of the bubbles was a maximum in the early states of the process. These conclusions are in good agreement with previous observations made by V. T. Slavyanskiĭ[62], who also emphasized a sequence in the gas fillings of seed bubbles from prevailing CO_2, to O_2 in the intermediate, and N_2 in the late periods of the fining processes. The experiments of Cable *et al.* did not immediately answer problems like those of volume changes, i.e., growth, shrinkage of the seeds during the heterogeneous gas reactions involved, and particularly not the possibilities for redissolution of gases in the liquid phase. In the second publication by Clarke and Haroon mentioned above, that portion of the complex problem was studied more specifically by systematic heat treatments, namely a longer exposure of the bubble-containing glass samples at 1200°C, then a controlled quenching, and cooling. A distinct difference was observed in the behavior of the As_2O_3-free melts and those to which As_2O_3 had been added: the first type of glass contained bubbles which did not strikingly change their volume and diameter, and in which the O_2 content slowly increased, whereas a glass to which only 0.1% As_2O_3 had been added showed bubbles which shrunk relatively rapidly, their gas content shifting more and more to O_2 enrichment. Evidently, an originally high CO_2 content was rapidly resorbed by the surrounding glass melt, and O_2 diffused into them. The principal effect of As_2O_3 is evidently an acceleration of the CO_2 resorption.

117. The observations of Cable and Haroon agree best with those of Slavyanskiĭ but are in other respects in contradiction with the results of Greene and Lee mentioned above (¶ 114). Nevertheless, there remain some open questions, e.g., on the origin of O_2 enriching in the gas bubbles, even when no As_2O_3 at all had been added. Another remarkable fact is the observation of F. L. Harding and R. J. Ryder[63] that an addition of Si_3N_4 to the batches of brown-colored (amber) glass distinctly controlled the S household in the glass, the solubility and distribution of the water content, the softening temperature, and the optical transmission data of the resulting glass products. Beyond that, the sulfate content in early melts influenced the solubility of N_2 in the glass, when compared with the behavior of analogous S-free glass, evidently by an energetic oxidation of Si_3N_4. Reaction of the nitride with sulfides was not directly observed but indirectly there was an accelerated reaction with carbon which then reduced the sulfate. Nitrides acted strongly reducing, evolving H_2 from chemically dissolved water, changing trivalent into divalent iron ions[64] cf. ¶ 212, 216).

[62] Oboronizd., Moscow, 1957, pp. 87–104.

[63] *Glass Technol.* **11**, (2), 54–58 (1970).

[64] One may compare the observations of T. H. Elmer and M. E. Nordberg, Proc. Int. Congr. Glass 7th, Bruxelles, 1965, Pap. 30, pp. 1–11, when glass melts are treated with ammonia gas.

Chapter III

Requirements That Must be Fulfilled by the Fined Glass before Working

STAININGS; COLOR CORRECTION (DECOLORIZATION)

118. The remarkable progress made in the last ten years in the investigation of the coloring principles in glass in compounds of heavy elements and specifically in the group of the transition elements of the Fe—Mn metals has much intensified the interest of the physical chemists in the subject. There is a rapidly increasing literature on the absorption and emission phenomena by classical spectroscopy in the visible, near-infrared, and near-ultraviolet ranges. This evolution parallels a rich literature in the field of optical crystallography of silicate minerals. Many newer publications are dedicated to investigations in the theoretical background, and numbers of them focus on problems concerning the application of the crystal field and the ligand theory (cf. Vol. VII. ¶ 678).

119. The investigator in colored-*glass* properties will therefore do well to study the boundary fields between silicate mineralogy and crystallography and glass research because both disciplines have so much in common regarding the methods and evaluation of measurement results of studies of the constitution of silicate crystal phases on one hand, glasses on the other hand. We recommend for these reasons a selection from more recent publications, including very instructive investigations made by W. B. White and K. L. Keester[1] on the absorption spectra of rock-forming Fe silicate minerals, namely actinolite, olivine, epidote, chlorite, and enstatite as paradigmata, over the spectral range from 400 to 3500 mμ, including the very important vicinity of the l-μ absorption band of divalent Fe, in sixfold coordination to oxygen. The authors see in their highly appreciated numerical and diagramatic results a confirmation of the hypothetic idea that Fe^{2+} cations may also occur in *tetrahedral* coordination, as indicated particularly by bands in the vicinity of the low-frequency end of the visible spectrum. These ideas formulated from the abundant

[1] *Amer. Mineral.* **51**, (5/6), 774–791 (1966).

numerical data by White and Keester, were critically discussed by W. H. Turner,[2] to which White and Keester answered.[3]

120. Of course, we see in the problems mentioned here of ionic color effects by Fe cations in silicate rock-forming minerals, preferably a highly valuable material for a comparison with our own aspects, and learn from the discussion of expert authors of mineralogical investigation tasks. We recall that in our discussions in Vol. VII (¶ 672, ff., 692 f. a. o.), we gave brief hints for an application of the ligand theory which we now have to transfer to more practical view points. Therefore, we recommend that the reader follow the discussions around the work done by White and Keester under the viewpoints given in the fundamental literature to be studied here:

C. J. Ballhausen, "Introduction into the Ligand Field Theory," McGraw-Hill, New York, 1962;

D. S. McClure, "Electronic Spectra of Molecules and Ions in Crystals," in "Solid States Physics in Chemistry," Section II, Spectra of Ions in Crystals, Academic Press, New York, 1959;

W. B. White cites in his answers to W. H. Turner further valuable literature on another limited field, namely, the "Optical Properties of Semiconductors", by T. S. Moss, Butterworth, London, 1961, and some of his investigations with R. Roy on the optical spectra of semiconducting transition metal oxides, which are in many cases of direct significance in comparison with glass containing transition metals, for their similarities and their differences.

121. Beyond this general introduction to our own problems, we see progress in the application of the tools of Mössbauer measurement techniques for a deeper going study of the nature of Fe in most diversified aspects in glass with a continuous comparison of what this elegant method can teach us from the analogous Fe silicate minerals in the crystallized state. In the special case of the discussions between White *et al.* and Turner (cf. ¶ 119 ff.), the Mössbauer analysis methods gave a clear answer insofar that the hypothesis of the tetrahedral coordination around the Fe^{2+} central cation is in its strict formulation untenable.[4] The spectral characteristics of Fe^{2+} may, with the same justification, be interpreted when the same cation is present in distorted octahedral coordination, equally for crystallized silicates, as in silicate glasses containing Fe.[5]

122. We include here reference to the importance of an elegant *polarographic*

[2] *Amer. Mineral.* **52**, (3/4), 553–555 (1967).

[3] *Amer. Mineral.* **52**, (3/4), 555–558 (1967).

[4] See R. G. Burns and G. M. Bancroft, *Amer. Mineral.* **52**, (9/10), 1278–1287 (1967).

[5] See also T. M. Dunn, D. S. McClure, and R. G. Pearson, "Aspects of the Crystal Field Theory," Harper & Row, New York, 1963.

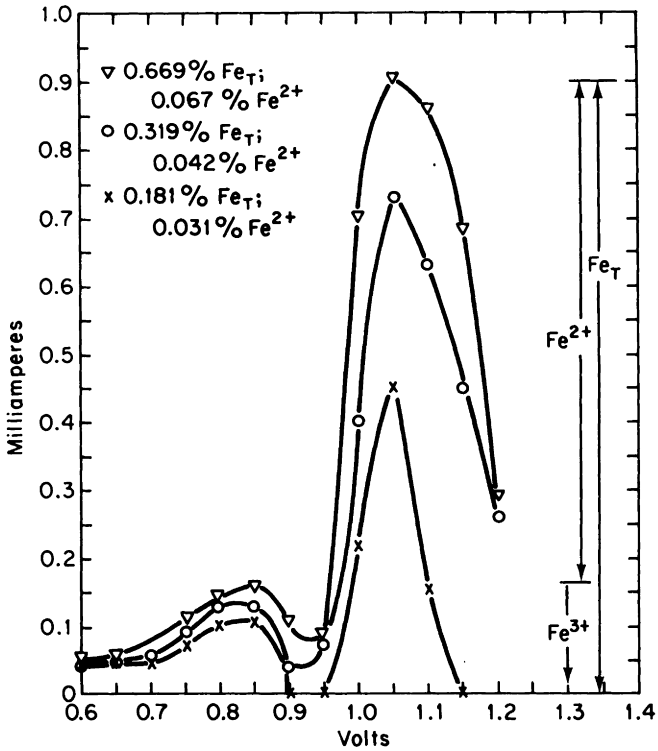


FIG. 24. Polarograms for iron in molten sodium disilicate. (Bååk and LaMar Frederick).

method introduced by Yu. K. Delimorskĭ, B. V. Markov,[6] and Yu. S. Lyalikov[7] then applied by Yu. K. Delimorskĭ and S. S. Ognyamk.[8] Tr. Baak and R. L. Frederick[9] demonstrated an application of this experience to studies on the behavior of Fe^{2+} and Mn^{2+} in melts of pure $Na_2O \cdot 2SiO_2$, for a fundamental correlation of the observed electrode potentials as a function of the concentration of the iron group metals on the surface of the electrodes, and their diffusion coefficients (following the Heyrovski–Ilkovic equation). The method itself is a modification of common voltametry, applying a rotating Pt electrode, for the study of minor additions to the silicate melt, behaving as an oxygen electrode. Bååk and Frederick derived from polarographs of the type as seen in Figs. 24 and 25 for Fe and Co, the instructive

[6] In "Electrochemistry of Fused Salts," Chapter VIII, Sigma Press Publ. Washington, D.C., 1961.
[7] *Zh. Anal. Khim.* **8**, 38–45 (1953).
[8] *Zh. Neorgan. Khim.* **7**, 1757–1761 (1962).
[9] *J. Amer. Ceram. Soc.* **50**, (1), 38–42 (1967).

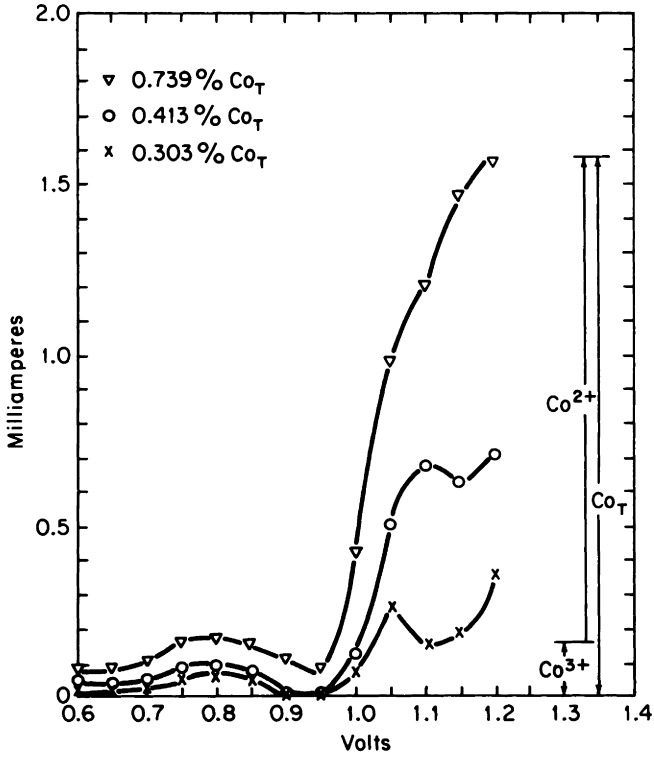


FIG. 25. Polarograms for nickel in molten sodium disilicate. (Bååk and LaMar Frederick.)

linear functions of the half-wave potentials, versus the concentration (in wt. %) for the cations of the transition element cations, (Fig. 26). The slope of the lines is indicative for the number, n of faraday units involved in the reduction reactions like, e.g.,

$$6\,e^- + Fe^{3+} + 3/2\,O_2 \rightleftharpoons FeO_3^{2+} \text{ with half-wave potential} = 1.01, \quad \text{slope } 0.040, \quad n = 6$$
$$3\,e^- + Fe^{3+} \rightleftharpoons Fe^0 \qquad = 0.74, \quad \text{slope } 0.084, \quad n = 3$$

but

$$e^- + Mn^{3+} \rightleftharpoons Mn^{2+} \qquad = 0.68, \quad \text{slope } 0.210, \quad n = 1$$

In sodium trisilicate glass of high purity degree, the ultraviolet absorption in the wavelength range from 190 to 360 mμ was determined by G. H. Sigel and R. J. Ginther[10] doping with Fe in oxidizing and reducing atmospheres: in the concentration range from 10^0 to 10^3 ppm absorption spectra are shown which were practically

[10] *Glass Technol.* **9**, (3), 66–69 (1968).

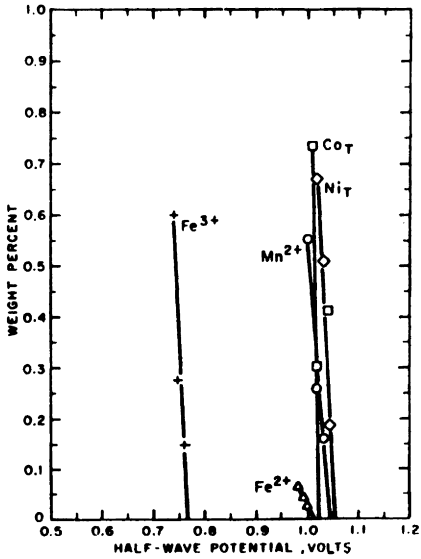


FIG. 26. Total concentration vs. half-wave potential for various ion valences. (Bååk and LaMar Frederick.)

independent of the melting conditions. Only for ultrahigh purity of the starting glass, an intrinsic edge at 195 mμ is observed. When Fe^{2+} or Fe^{3+} ions are present, these contribute shiftings of the absorption edge to longer waves. By electron paramagnetic resonance as a measure of concentration in Fe^{3+} the molar extinction effects could be established. The characteristic maxima of absorption bands intensities are found for Fe^{3+} at 225 mμ, for Fe^{2+} at 205 mμ (cf. Figs. 27 and 28).

123. Quantitative determinations of the oxidation–reduction equilibria for the oxides of Fe, Mn, V, Cr; S, Se; Sb, As; Ti, Sn, U, in concentration down to a few ppm in the samples were extensively discussed by W. P. Close and J. F. Tillman[11], alone and in combinations of those elements, with particular consideration of those which develop such coloring effects in glass as Cu-red, Mn-brown, ultraviolet absorption in green glass, and Fe sulfide brown (amber), or Se "rosaline" glass tints. They used potentiometric titration, redox reactions (e.g., an Fe–Cr method) for an estimation of Cu^{2+}, Mn^{3+}, Cr^{6+}, Sn^{2+}, and common chemical separation methods. If two or more elements are present in two or more different oxidation states, and if in addition the redox potentials are sufficiently different (cf. single electrode potentials determined in aqueous solutions), then as a rule, only one of those elements concerned will be present in more than one oxidation state, and only one of the redox systems

$$Fe^{2+} \rightleftharpoons Fe^{3+} + Cr^{3+}; \text{ or } Fe^{3+} + Cr^{3+} \rightleftharpoons Cr^{6+}$$

[11] *Glass Technol.* **10**, (5), 134–146 (1969).

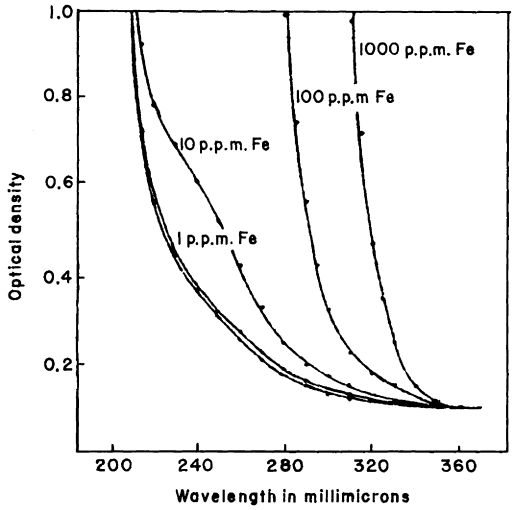


FIG. 27. Effect of iron concentration on the position of the ultraviolet absorption edge in 1.0 Na_2O, 3.0 SiO_2 glass, melted in oxidizing atmosphere; samples were 1.0 mm thick. (Sigel and Ginther.)

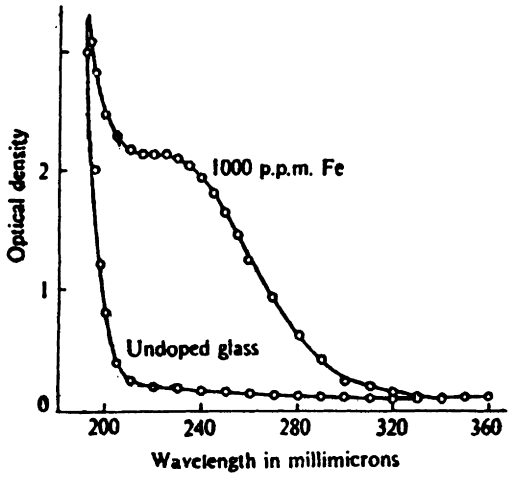


FIG. 28. Ultraviolet absorption of undoped and iron-doped glass, melted in oxidizing atmosphere (sample thickness was 0.05 mm). (Sigel and Ginther.)

will appear, but not

$$Fe^{2+} = Fe^{3+} + Cr^{3+} = Cr^{6+}$$

A unique exception was observed in a glass containing the redox pair

$$Cu^{2+} = Cu^{+} + V^{5+} = V^{4+}$$

when the glass was melted in open air. Polarographic methods are very suitable for the control of oxidation steps, when using the Beckman Electroscan 30 in conjunction with a Sargent mercury dropping electrode.[12]

124. From the more practical point of view, G. Paoletti and L. Amati[13] gave valuable advice for the measurement of the "color degree" or "lack of color" of industrial glass production, with a more or less developed greenish tint caused by iron contamination. For the quantitative control of suitable decolorization treatments the measurement of the tint intensities can be made with relatively thin samples (thickness may be down to 2 mm), by applying a high sensitivity in optical photometry and using a set of standard color filters of different wavelengths in the visible range (a "decolorimeter"). For more accurate measurements of the color by trichromatic instrumentation, A. R. Koenig[14] recommends a combination with a computer unit and a corresponding program, for rapid and precise results.

125. Equally, for a color definition in the Helmholtz color triangle projection, G. Heuthe[15] presented a full introduction into the coloring nature of CoO, NiO, CuO, and Cr_2O_3 from older data of H. Hennig, with special reference to the color definitions of those oxides by the System of the Commission Internationale de l'Éclairage "*CIE*"[16] and FeO in concentration steps up to 4.5% in normal Na–Ca silicate glass, and its transmissivity in the range from 400 to 700 mμ, using the UNICAM SP to spectrophotometer. Rich tabulated data combined with color curves in rectangular planar graphs were presented for controlled ratios of the $FeO:Fe_2O_3$ contents. The higher the reduction degree, the more the representing points of the colored-glass samples appear to shift towards the blue apex of the color field. The staining effects of Fe and Co are additive, the representing points of mixed colors being projected in approximately parallelogrammatic fields, inside the enveloping curves of the effects of the pure oxides. Diagrams of this kind are successfully applied to problems of decolorization of Fe-containing glasses, either by physical correction, i.e., by additions of Se, Co, or Ni, or chemically by addition of MnO_2, As_2O_3, or CeO_2.

126. In the foreground of our practical concern must, of course, stand the conditions of redox equilibria of the *iron oxides* in silicate glasses. Among the abundant publications in this wide and extremely important special field, we first selected the following results of recent extensive investigations:

[12] Cf. Tr. Bååk and E. J. Hornyak, *J. Amer. Ceram. Soc.* **44**, 541–544 (1961); cf. Vol. II.B. ¶ 48, footnote number 63; this volume ¶ 98.

[13] *Vetro Silicati* **7**, (38), 5–9 (1963).

[14] *Glass Ind.* **47**, (12), 676–680 (1966).

[15] *Silikattechnik* **18**, (9), 279–281 (1967).

[16] *Glas Email Keramo Tech.* **15**, 397–409 (1964).

Based on very early investigations of Cl. Kühl, H. Rudow, and W. Weyl,[17] H. J. Trees[18] developed thermodynamic approximation calculations for the oxygen dissociation pressures of glass-forming oxides, specifically for metals with variable valencies, i.e., in the first line Fe, but also Mn, Cr, As, Sb, Sn in pairwise solid redox oxides which we mentioned above. These calculations were based on tabulated standard values for $\Delta G°$, $\Delta H°$, and $\Delta S°$, to a sequence of decreasing dissociation pressures p_{O_2}. Specifically for Mn, however, discrepancies were detected which could only be overcome when experimental and industrial glasses also contain higher oxides than Mn_2O_3 persisting. An orienting graphic diagram Fig. 29 may illustrate

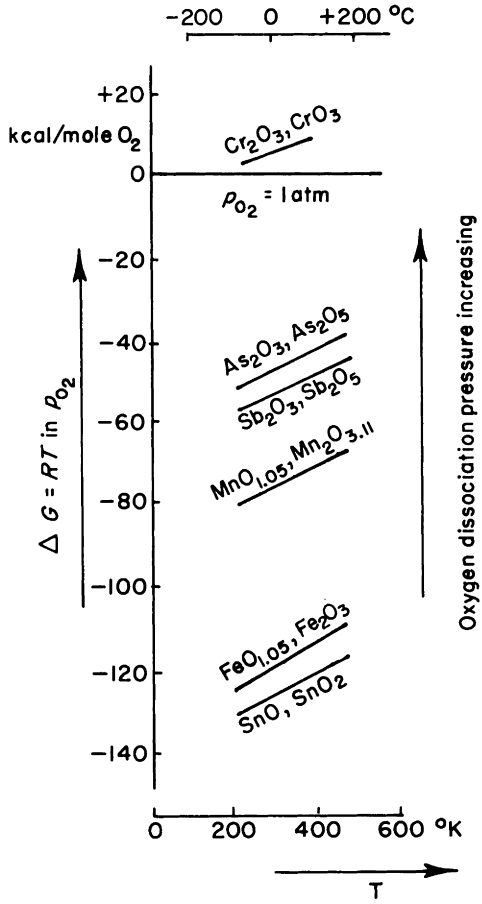


FIG. 29. Graphs relating p_{O_2} to temperature for pairs of solid redox oxides. (Tress.)

[17] *Sprechsaal* **71**, 91–93 (1938); **71**, 104–106 (1938); **71**, 117–118 (1938).
[18] *Phys. Chem. Glasses* **1**, (6), 196–197 (1960).

the pairwise solid redox oxides in their parameters $\Delta H = RT \ln p_{O_2}$, plotted versus T as the coordinates.

127. Fundamental investigations of the oxidation–reduction equilibria in Fe-containing $Na_2O \cdot 2SiO_2$ glasses were more recently made by W. D. Johnston.[19] When the $-\log p_{O_2}$ is plotted in a diagram versus the log ratio (Fe^{2+}/Fe^{3+}), the equilibrium of the reactions

$$4Fe^{3+} + 2O^{2-} = 4Fe^{2+} + O_2$$

is established and shifted to the right-hand side of the equation with increasing temperature. The reaction itself is highly sluggish until final equilibria are reached; the mechanism is diffusion controlled. When the experiments were made in Pt crucibles, considerable amounts of Fe were alloyed into the crucible walls; for this reason the use of sintered alumina crucibles was indispensable. Fe metal is precipitated from the glass melts when the reduction degree is higher than 90%; after having passed this limit the ratio Fe^{2+}/Fe^{3+} is no longer functionally dependent on $\log p_{O_2}$. It is noteworthy that Tr. Bååk and E. J. Hornyak[20] gave data in their lower temperature measurements under the same equilibria conditions but when the experiment was worked in alumina crucibles, they also gave data for $-\log$(ratio Fe^{2+}/Fe^{3+}) which are considerably different from those of Jonston (cf. Fig 30) although above 1200°C the results of the two experimental series probably agree. We are inclined to join the opinion of Johnston that the reaction time periods chosen by Bååk and Hornyak were too short to have reached real equilibria. The low parameters $\Delta H°$ derived from their experimental data in Fig. 30 give rise to an entropy term of a different sign from that found by Johnston (he gave +log kcal/mole). We will come back to these first results somewhat later when we have to discuss another publication of W. D. Johnston's on oxidation–reduction equilibria of the oxides of Ti and V, in comparison to those of Fe, Co, and Ni[21] (cf. ¶ 145). Then we also have to speak of W. D. Johnston's and A. J. Chelko's investigations on the reduction of Fe ions in glass by hydrogen, for a comparison with analogous reactions with the ions of Ce and Sn.[22]

128. When the high requirements of optical homogeneity, and a colorless light transmission in the technology of the production of *optical glass* must be fulfilled,

[19] *J. Amer. Ceram. Soc.* **47**, (4), 198–201 (1964).

[20] *J. Amer. Ceram. Soc.* **44**, (11), 541–544 (1961).

[21] Cf. *J. Amer. Ceram. Soc.* **48**, (2), 184–190 (1965); on the formulation of the oxidation–reduction reactions see specific notes by W. D. Johnston, *ibid.* **48**, (4), 228–229 (1965); the latter concerning a calculation of relative oxygen ion activity of the base glass.

[22] *J. Amer. Ceram. Soc.* **53**, (6), 295–301 (1970).

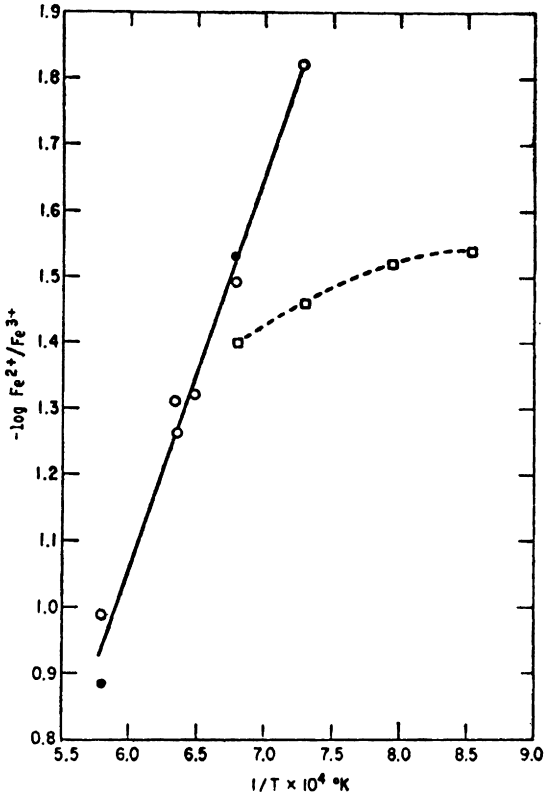


FIG. 30. Dependence of Fe^{2+}/Fe^{3+} ratio on temperature for samples equilibrated in air. ○: Al_2O_3 crucible; ●: Pt crucible; □: Bååk and Hornyak. (Johnston.)

the highly critical task is in most cases the accurate determination of *trace elements* which cause anomalous staining tints. Here, of course, not only Fe is to be considered as an undesirable contamination, so is the presence of Mn, Co, Ni, Ti, V, Cr, and the platinum metals, perhaps also the presence of rare-earth elements when special highly refractory container materials must be used. Contaminations of such a type in trace concentrations down to 0.01% may still cause distinct staining effects. D. E. Campbell and P. B. Adams[23] emphasize that in the place of and at least for supplementation of classical chemical-analytical methods, modern physical tools must be applied, e.g., the technologies of neutron activation, X-ray emission, mass spectrometry, flame emission techniques, atomic absorption spectrophotometry,

[23] *Glass Technol.* **10**, (2), 29–34 (1969), with a rich bibliography.

and galvanic, polarographic, and coulometric methods in order to master the multiplicity of problems arising in tracer determination. In many cases it may be sufficient to select among these possibilities some combinations of more elementary methods—in most cases optical emission spectroscopy with refined colorimetric techniques.

129. A very interesting special case of staining and decolorization reactions in *silica glass* which is, as commonly known, stained brown rather rapidly by a treatment in Na vapor at 250° to 500°C, presumably by electron trapping in quite distinct sites, was observed and completed by J. A. Burns.[24] The role which trapped Al sites may play in these reactions is not yet sufficiently clear.[25] At the same time, a second, considerably slower decolorization *bleaching* process superimposes in which the color centers are resorbed and evidently assimilated into the structure of a Na–silicate glass "dissolved" in the surrounding silica glass to a homogeneous phase. These highly troublesome staining effects for the useful service lifetime of Na vapor discharge lamps raise problems for the development of new special glasses which must be more resistant to the attack by Na vapor.

COLOR EFFECTS CAUSED BY TRANSITION ELEMENTS

130. Specifically for iron, magnetic properties of different ions in the formation of staining oxides and *ferrites* may be applied for the study of the dispersed states in such systems. R. R. Shaw and J. H. Heasley[26] described the super-paramagnetic behavior of finest particles of α-Fe_2O_3 or $MnFe_2O_4$ from silicate melts, and M. P. Borom[27] used the electron-beam microprobe techniques for the study of the diffusion of Fe metal into $Na_2O \cdot 2SiO_2$ melts at 900° to 1050°C. He also used measurements of the light transmissivity and of magnetic susceptibility to identify at 900°C, only Fe atoms, and at 1050°C, Fe cations, as the diffusing units. These methods of high sensitivity recall somewhat the performance of the experiments on the production of luster glasses, by surface diffusion of metal deposits into the glass surface, as described by Z. Cozl-Zrustek.[28]

131. From the experience of mineralogy and petrology, it is certainly interesting that in volcanic glasses it was possible by systematic measurements of the refractive

[24] *Glass Technol.* **6**, (1), 17–21 (1965).

[25] See also A. Kats and J. M. Stevels, *Philips Res. Repts.* **11**, 115–156 (1956); J. W. Wheeldon, *Brit. J. Appl. Phys.* **10**, 295–298 (1959).

[26] *J. Amer. Ceram. Soc.* **50**, (6), 297–302 (1967).

[27] "Diffusion of Iron into Sodium Disilicate Glasses," Washington, D.C. Office Techn. Service, 1963, Documt. UCRL, AEC Contract No. W. 7405 Eng. 48; *Phys. Chem. Glasses* **8**, (5), 203–205 (1967).

[28] Sym. on Colored Glass, Prague, Int. Comm. Glass, Prague, Sept. 1967, pp. 374–389; see *Glastech. Ber.* (abstract) **41**, (6), 259 (1968).

indices as a function of oxygen fugacity by R. F. Fudali,[29] and later by M. Carapezza[30] to demonstrate in a graphic projection a slope of $-\frac{1}{4}$ for the Flood reaction[31]: $4FeO + O_2 \rightleftharpoons 4FeO_{1\frac{1}{2}}$. The diffusion of Fe cations in melts of Na Silicate glasses (with 20 to 50 mole % Na_2O) in air atmosphere was also determined by M. L. Pearce and J. F. Beisler,[32] with the important result that in the system Na_2O-SiO_2-FeO (in air atmosphere, and at 1200°C const.) the diffusion coefficients were in the range from 10^{-5} to 10^{-8} cm²/seconds when the Na_2O content was lower than 30 mole % (cf. Figs. 31 and 32).[33]

132. A comprehensive examination of the Fe^{2+}/Fe^{3+} equilibria in binary alkali

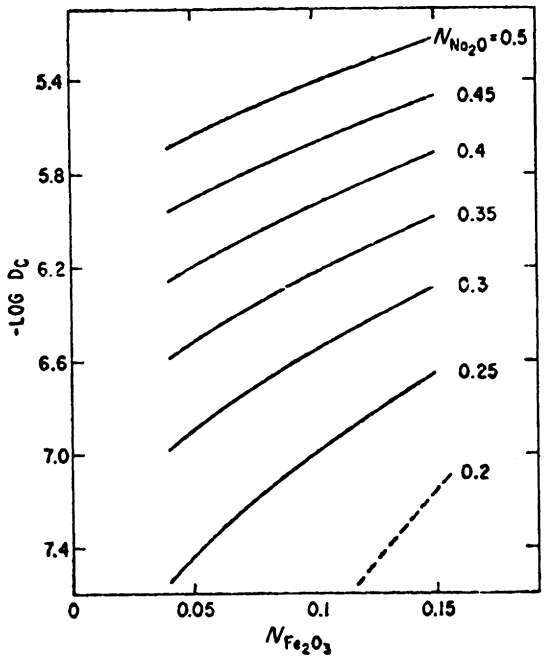


FIG. 31. Variation of log diffusion coefficient with mole fraction ferric oxide in the ternary melt of system $Na_2O-Fe_2O_3-SiO_2$, for variable values of N_{Na_2O}. (Pearce and Beisler.)

[29] *Geochim. Cosmochim. Acta* **29**, 1063–1075 (1965).

[30] *Atti. Accad. Naz. Lincei Cl. Sci. Fis. Mat. Natur. Rend.* **40**, 970–978 (1966); *Acta Mineral. Petogr.* (Bologna) **12**, 181–193 (1966) (with R. Mezzetti), based on a linear correlation of p_{O_2} and the log ratio $FeO/FeO_{1\frac{1}{2}}$.

[31] Cf. Fudali, *Atti, Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nature. Rendicanti.* **40**, 1071 (1966).

[32] *J. Amer. Ceram. Soc.* **49**, (10), 547–551 (1966).

[33] On the diffusion in slag melts cf. Vol. II.C. ¶ 86, 104.

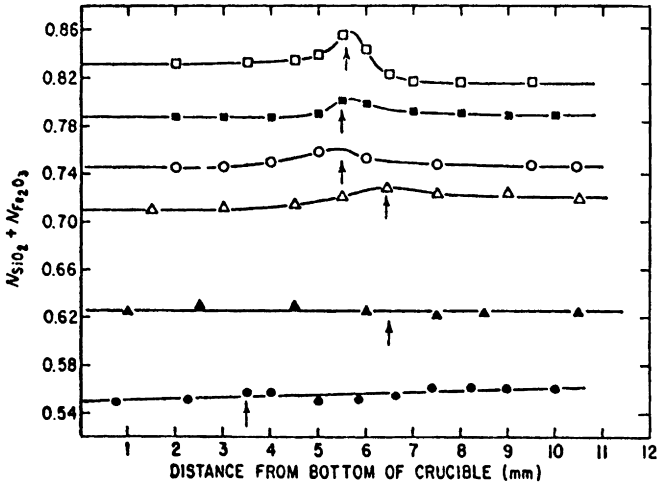


FIG. 32. Silica and ferric oxide concentration profiles for melts of varying basicity. (Pearce and Beisler.) The arrows indicate location of original interface.

silicate glasses with 10–40 mole % R_2O and 60–90 mole % SiO_2 (R = Li, Na, K), and 0.5 mole % FeO, at 1400°C, was performed by A. Paul and R. W. Douglas.[34] The equilibria were reached at 1400°C for a l-cm-thick layer of 30-g glass in 70–150 hours. Then, the melts were quenched from the liquid state, and the equilibrium concentrations determined by chemical analysis. For a glass with 10% K_2O it corresponded to ~45/55, for another glass with 30% K_2O ~ 8/92. We refer to previous observations that less than 30% R_2O is a kind of critical limit for reactions of the glass with the walls of Pt crucibles, in which Pt acts as an oxidizing agent on the equilibrium conditions, but does not do so for more than 30% alkali. On the other hand, sintered alumina crucible walls react with melts containing more than 15%. For this reason, Paul and Douglas worked with silica glass containers (Fig. 33), in spite of the considerable corrosion effects by the silicate melt. The ratio Fe^{2+}/Fe^{3+} is also influenced by Fe concentrations above 5 wt. %; with increasing basicity of the melts, either by introduction of more alkali, or by substitution of Li by Na, of Na by K, the equilibria are shifted to the Fe^{2+} side (cf. Figs. 34 and 35).

133. Again, we recommend in every way for studies of Fe in its versified physical correlations to glass, experimental, and industrial as they may be, the importance of R. L. Mössbauer's elegant methods now combined with his name, as a phenomenon of nuclear absorption spectroscopy. In order to avoid repetitions we will select from

[34] *Phys. Chem. Glasses* **6**, (6), 207–211 (1965).

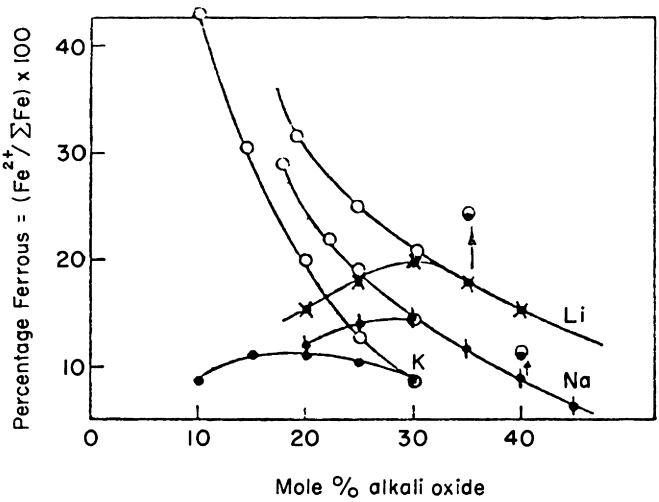


FIG. 33. Equilibrium Fe^{2+} content in binary alkali silicates at 1400°C melted in crucibles of different material. ○: melted in silica; ●: melted in platinum; ⊖: melted in alumina. (Paul and Douglas.)

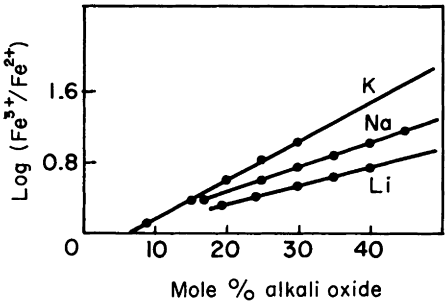


FIG. 34. Variation of iron equilibrium with alkali concentration in binary alkali silicates. (Paul and Douglas.)

our previous text the literature in this wide field of intense research endeavours mostly in reference to the texts mentioned in Vol. VII, introduced by the highly recommendable original article of the discoverer himself,[35] and then the more specialized articles by G. K. Wertheim.[36]

134. With special regard to the importance of the Mössbauer method for glass

[35] *Naturwissenschaften* **50**, (7), 282–290 (1963).

[36] *Science* **144**, (3616), 253–259 (1964); and his book publication "Mössbauer Effect. Principles and Application," Academic Press, New York, 1964.

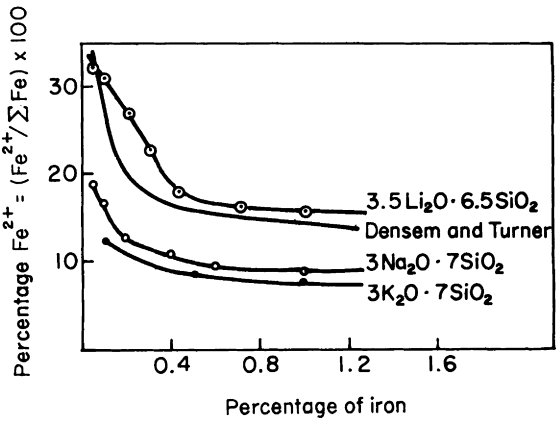


FIG. 35. Effect of total iron concentration on the ferrous–ferric equilibrium in alkali silicate glasses. (Paul and Douglas.)

research in general, and for Fe^{57}-colored glasses in particular, we emphasize the excellent publication by C. R. Kurkjian and D. N. E. Bughanan.[37] In this report, $Fe(PO_3)_3$ and $Na_2O \cdot 3SiO_2$ glasses, containing 0.1 to 5.0% Fe_2O_3 which are paramagnetic [crystalline $Fe(PO_3)_3$ is antiferromagnetic below 10°K], were examined. The glasses showed a magnetic hyperfine split (hfs) spectrum, with exception of that containing 5% Fe_2O_3 in $Na_2O \cdot 3SiO_2$ matrix. Probably, the electron spin relaxation time is long in comparison with the magnetic hyperfine interaction. Both Fe^{2+} and Fe^{3+} cations are in octahedral coordination. Line widths of 0.065 to 0.075 cm/second were obtained in comparison with 0.055 cm/second in the crystalline phases. The quadropole splitting for Fe^{3+} is considerably larger than for the crystalline state; the nonidentical sites in the glasses are more distorted than they are in the crystal phases (cf. Fig. 36 and Fig. 37). They show the influence of temperature on the spectra for glasses and crystal phases. Interesting is a comparison of Mössbauer spectra of Fe silicate *minerals* (including Fe pyroxenes, and cummingtonite-grunerite amphiboles), as studied by G. M. Bancroft and R. G. Burns.[38] (Cf. Vol. VI.A ¶ 141 ff., 166 ff.)

135. Analogous investigations on the Mössbauer spectroscopy of Fe—Na silicate glasses by G. Tomandl, G. H. Frischat, and H. J. Oel[39] show the phenomena of

[37] *Phys. Chem. Glasses* **5**, (3), 65–70 (1964); with a very valuable list of special references.

[38] Mineral. Soc., Miner Int. Assoc., Proc. Paps., Gener. Meetg., 5th, Cambridge, 1966 (publ. 1968), pp. 36–42; Amer. Miner. **52**, (7/8), 1009–1026 (1967) on amphiboles.

[39] *Glastech. Ber.* **40**, (8), 293–298 (1967).

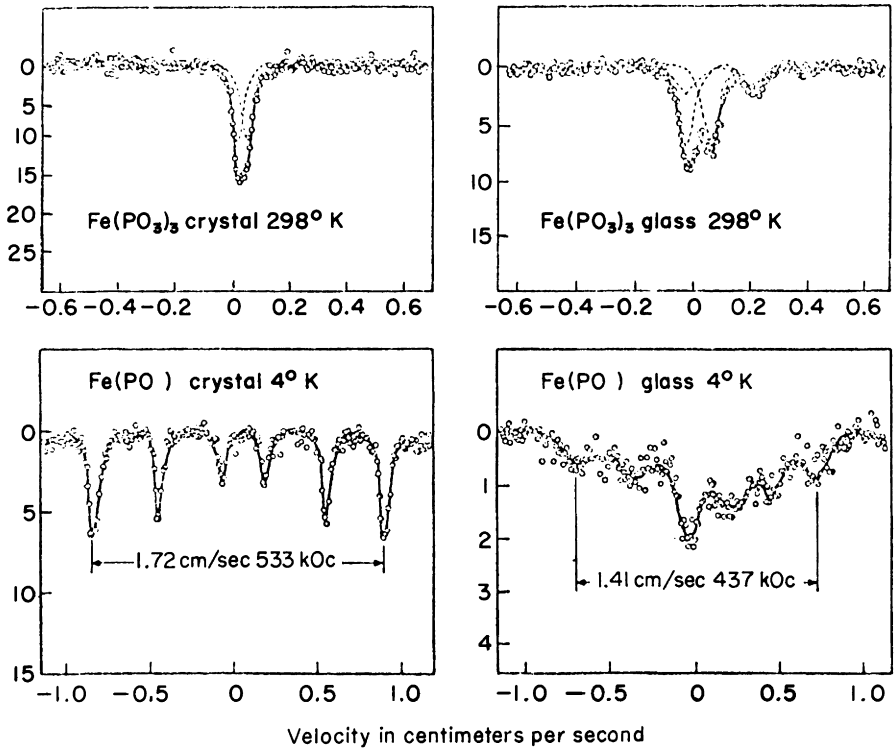


FIG. 36. Mössbauer spectra of glassy and crystalline ferric metaphosphate; source is $CuCo^{57}$. (Kurkjian and Buchanan.)

isomeric shifting, quadrupoles splitting, and sixfold magnetic splitting, also line-widening effects, in agreement with the recoil resonance theory. Interesting is the experimental use of amplifying multiscale and multichannel instrumentation with a scintillation counter system, in the place of the elementary mechanical systems of previous measurements, calibrated by the spectra of $K_4Fe(CN)_6 \cdot 3H_2O$, in comparison with $Fe(COO)_2 \cdot 2H_2O$, and $Fe(NO_3)_2 \cdot 6H_2O$, and with the effects of systematic changes of the Fe^{2+}/Fe^{3+} ratios by a thermal (oxidation–reduction) treatment in controlled atmospheres. Annealing of the glasses is without any influence on the character of the Mössbauer spectra, however. As an example of the achievement reached in the spectra obtained of different glasses with varying ratios Fe^{2+}/Fe^{3+} we present Fig. 38. The same authors[40] used Mössbauer spectroscopy for an experimental determination of the valence ratios and the coordination states of Fe-

[40] *Glastech. Ber.* **42**, (5), 182–185 (1969).

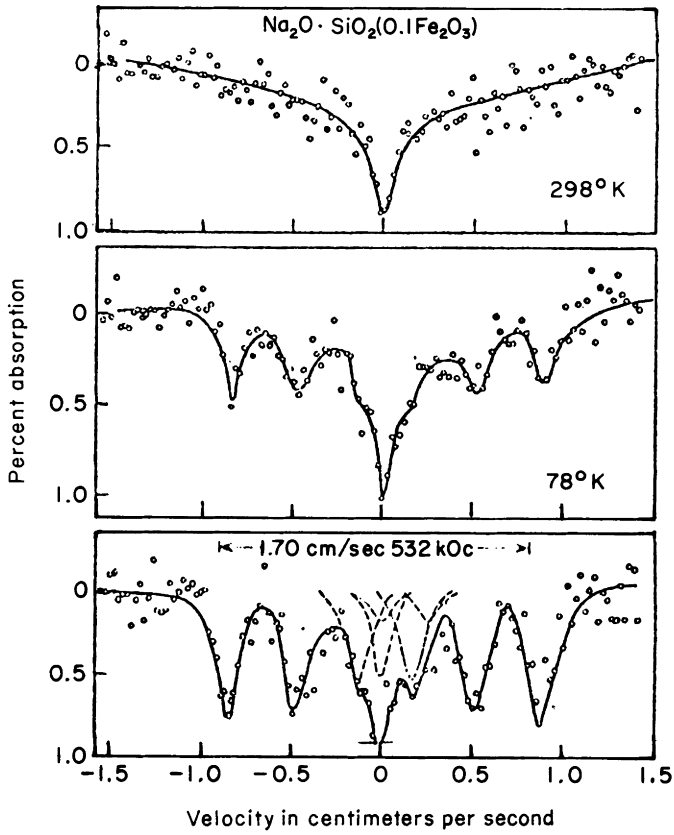


FIG. 37. Mössbauer spectra of $Na_2O \cdot 3SiO_2(0.1Fe_2O_3)$ as a function of temperature, source $CuCo^{57}$. (Kurkjian and Buchanan.)

containing silicate glasses, by a refined electronic computer calculation, and the least-square method. In a series of experimental Fe(III) silicate glasses with an Fe_2O_3 content between 2 and 18 mole %, a critical limit was reached for the transition of $[FeO_4]$ into $[FeO_6]$ coordination when the molar ratio $Fe^{3+}/[(Na^+ + \frac{1}{2}Ca^{2+}) + Fe^{3+}]$ is larger than 0.5. This threshold is indicated by an isometric shifting of the Mössbauer effect, namely, by a change of (4A) electrons in the cationic configuration.[41] For Fe–*phosphate* glasses no analogous transition in coordination was observed, because in these the $[FeO_6]$ coordination is *a priori* dominant.[42] Figure 39 shows three inner doublets, the two inner doublets being to Fe^{3+} in tetrahedral

[41] Cf. L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Lett.* **6**, 98–101 (1961).
[42] Cf. C. R. Kurkjian and A. E. Sigety, *Phys. Chem. Glasses* **9**, (2), 73–83 (1968).

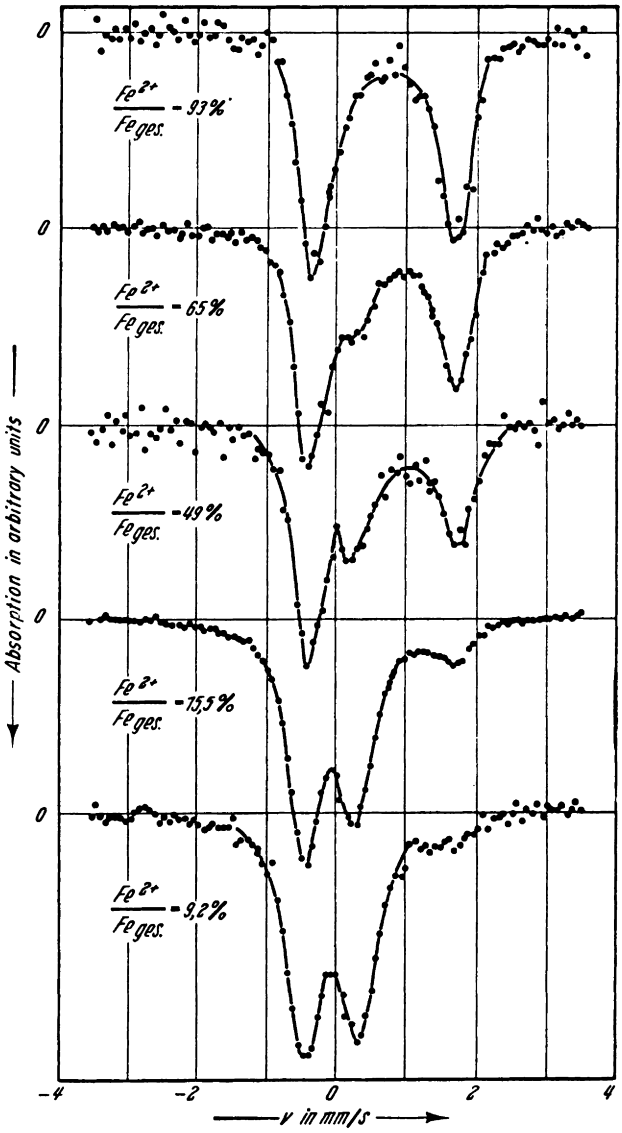


FIG. 38. Mössbauer effect for a silicate glass at variable ratios Fe^{2+}/Fe^{3+}. (Tomandl, Frischat, and Oel.)

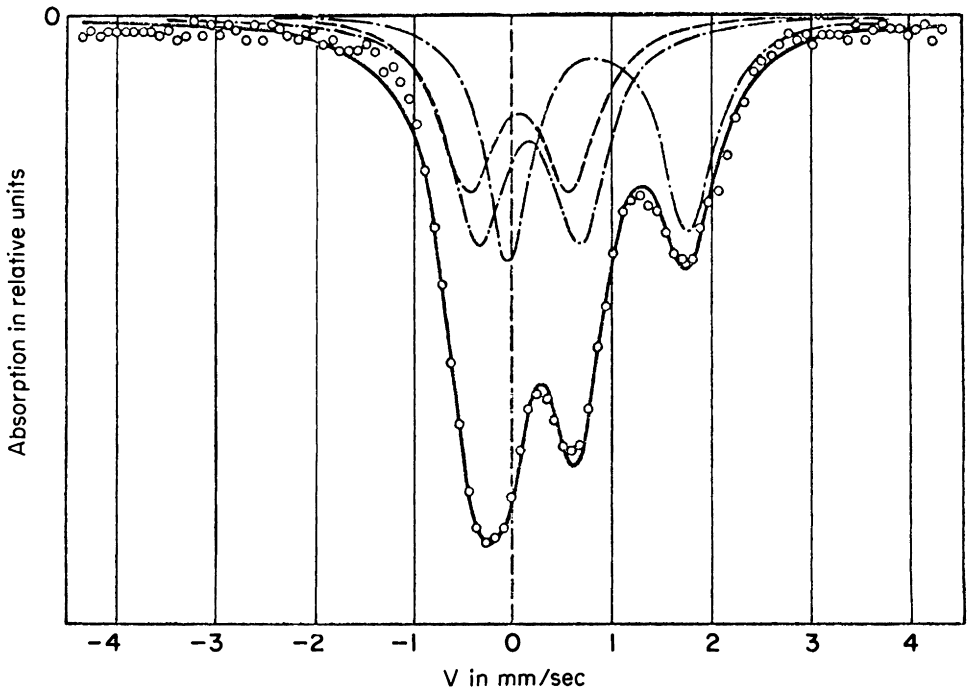


FIG. 39. Mössbauer spectrum of an iron-alkali silicate glass (5 mole % Na_2O, 5 mole % CaO, 16 mole % Fe_2O_3, 74 mole % SiO_2) for discrimination of tetrahedral and octahedral coordinated Fe^{2+} and Fe^{3+} cations. (Frischat and Tomandl.)

coordination; the exterior doublet to Fe^{2+}. The ratio of the area for the two inner doublets and the equilibrium ratios for the change from four- to sixfold coordination is 1.13[43] for observations at room temperature. The Mössbauer spectra changed in the shape and width of the lines with increasing concentrations in Fe_2O_3. Such glasses are paramagnetic at very low absolute temperatures.

136. On electron spin resonance absorption of Fe^{3+}, the linewidths, intensities, and g values have been systematically investigated as a function of the content of alkalies, and of Fe^{3+} for Na – Ca borate glasses as a matrix, but also for silicates and phosphates, by D. L. Loveridge and S. Parke,[44] and the resonance effect for $g = 4.3$ in comparison with changes in the ultraviolet charge transfer and ligand field bands. This is explained by the origin of the electron spin resonance from the ground-state

[43] See also a recent publication G. H. Frischat and G. Tomandl, *Glastech. Ber.* **44**, (5), 173–177 (1971).
[44] *Phys. Chem. Glasses* **12**, (1), 19–27 (1972)(cf. Vol. VII. ¶ 703 f.).

splittings which is sensitive to details of symmetry. Optical spectroscopy is not able to reveal such particular conditions. Some special assumptions are to be made when electron spin resonance results are to be tentatively interpreted on a structural basis. It is not possible to apply the resonances at $g = 4.3$ and $g = 2.0$ (the latter at high concentrations in Fe) as indicators of tetrahedral and octahedral coordination. S-containing amber glasses show an absorption at $g = 6$, in addition. For the isoelectronic Mn^{3+}, the $g = 4.3$ resonance is smaller, and less well observed than that for Fe^{3+}, but a large one is again observed at $g = 2$, often with a hyperfine structure. Cr^{3+} in phosphate glasses gives resonances for $g = 2$ to 6 (cf. Figs. 40 and 41).

137. Supplementing this, we also mention investigations made by A. M. Bishay and L. Makar,[45] on Fe staining of Ca phosphate glasses, containing stepwise increas-

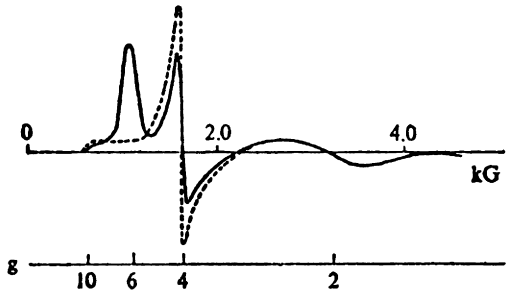


FIG. 40. Electron spin resonance spectra of Fe^{3+} in $30K_2O$, $70SiO_2$ amber glass at 9325 Mc/s, 77° and 295°K. (Loveridge and Parke.) Full lines: 0.1 wt. % Fe^{3+}; 3.0 wt. % S (in batch); broken lines: 0.1 wt. % Fe^{3+}; no sulfur in glass batch.

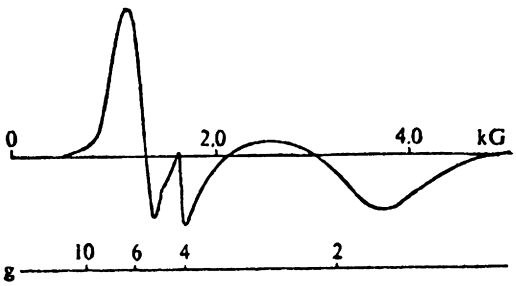


FIG. 41. Electron spin resonance spectrum of Fe^{3+} in the same amber glass, but a higher proportion of sulfur. (Loveridge and Parke.)

[45]Symp. on Coloured Glass, Int. Comm. Glass, Prague, Sept. 1969; pp. 210–226; *J. Amer. Ceram. Soc.* **52**, (11), 605–609 (1969).

ing 0.5 to 26 mole % Fe_2O_3, concerning their infrared absorption characteristics, electrical conductance, electron spin resonance spectra, and magnetic susceptibility, in both the glassy state and in recrystallized samples. The electron spin resonance measurements confirm the simultaneous presence of Fe^{3+} and Fe^{2+} cations, in tetrahedral and octahedral coordination, with more than 6% Fe_2O_3. In the same measure as the Fe_2O_3 concentration is increased, the ratio of Fe^{2+} in the four- and sixfold coordination is decreased, as was concluded from the intensity changes in the optical absorption bands at 2- and 1-μ wavelength. The spin resonance data for $g = 4.26$ and $g = 2$ confirm, on the other hand, how the ratio of tetrahedral and octahedral coordination is decreasing with increasing contents in Fe. In the same time, the electric conductance and the activation energy are decreasing. When the glasses are γ-irradiated with a high-intensity source of Co^{60}, the ratio Fe^{2+}/Fe^{3+} is reduced.

138. Another investigation series on iron spectra from alkaline earth phosphate glasses by C. Hirayama, J. A. Castle, and M. Kuriyama,[46] including optical absorption spectroscopy, electron spin resonance, and Mössbauer techniques data, was already discussed in Vol. VII. ¶ 767, and may therefore be mentioned here only briefly.

138a. Analogous studies on *manganese* Mn^{2+} as the coloring cation in silicate, borate, and phosphate glasses, by K. B. Bingham and S. Parke[47] also include studies on the visible *fluorescence* bands, in comparison with those of MnF_2 and the $Mn(H_2O)_6^{2+}$ ion for which the ligand theory could be applied (cf. Vol. II.A. ¶ 350). Of practical interest are the strong differences in the fluorescence colors (red for the phosphate glasses, orange for borate, green for silicate glasses) and superposition (additivity) phenomena observed in a borosilicate matrix. The fluorescence is in its maximum intensity in a quite distinct concentration of Mn^{2+}, e.g., of 1 mole % for silicate glasses. A. Paul[48] studied, on the other hand, the optical absorption of Mn^{3+} containing alkali borate glasses (cf. Vol. II.A. ¶ 350). The equilibria between the Mn^{2+} and Mn^{3+} cations in alkali borates are a function of the alkali (R_2O) contents in a linear correlation of $\log(Mn^{2+}/Mn^{3+})$ to the mole % concentration in alkalies (cf. A. Paul and A. Lahiri).[49]

139. Numerous special investigations have been dedicated to problems of *chromium* coloration in glasses, particularly of the equilibrium between Cr^{3+} and Cr^{6+} cations, e.g., in alkali silicate glass matrix. We mention here in the first place

[46] *Phys. Chem. Glasses* **9**, (4), 109–114 (1968).
[47] *Phys. Chem. Glasses* **6**, (6), 224–232 (1965).
[48] *Phys. Chem. Glasses* **11**, (5), 168–173 (1970).
[49] *Jour. Amer. Ceram. Soc.* **49**, (10), 565–568 (1966).

studies by P. Nath, A. Paul, and R. W. Douglas.[50] At 1100°C the equilibria in a 0.1 mole % Cr_2O_3-containing $3Na_2O \cdot 7SiO_2$ glass is established after about 90 hours in air atmosphere, with a final ratio Cr^{3+}/Cr^{6+} of 17/83. The equilibria are much more rapidly reached in the direction $Cr^{6+} \rightarrow Cr^{3+}$ than in the opposite one. At 1370°C the corresponding time to reach equilibrium is 50 hours, the final ratio Cr^{3+}/Cr^{6+} is 45/55. For the spectroscopic control the band at 650 mμ is particularly suitable, for Cr^{6+} the ultraviolet band 370 mμ. There is a shifting to higher contents in Cr^{6+} with increasing alkali concentrations for Li_2O, Na_2O, K_2O. It is of practical importance that the simultaneous presence of Fe develops the green color of the very popular "emerald" container glasses. The ultraviolet band at 370 mμ corresponds to the maximum photochemical food deterioration effect. R. C. Knupp and D. E. Berger[51] studied this problem extensively and observed that the presence of Fe (introduced as magnetite) causes a shifting of the Cr absorption band in the measure as the ratios Cr^{3+}/Cr^{6+}, simultaneously the ratios Fe^{2+}/Fe^{3+}, and the temperature and duration of the glass melting process, which exposes the glass to the furnace atmosphere, are changed. An excess sulfate content in the glass batches has a pronouncedly unfavorable influence on the absorption in such emerald green container glass products by a diminished absorption in the ultraviolet range.

140. More recently, P. Nath[52] published a comprehensive report on the Cr^{3+} – Cr^{6+} equilibrium with binary alkali borate glasses as the matrix, and in comparison with the investigations of the same author with R. W. Douglas *et al.* (see ¶ 139). Although only very small amounts of Cr are dissolved in pure B_2O_3 glass, more than 90% of this Cr is present in the six-valent state. Then when, e.g., Li_2O is added up to 25 to 30 mole % Li_2O the proportion of Cr^{6+} gradually decreases, then progressively increases. Analogous reactions were observed in borosilicate glasses colored by Cr^{3+}/Cr^{6+} up to 10 to 15 mole % Na_2O, with Cr^{6+} decreasing but above this limit concentration of Na_2O was in the reversed direction. The same phenomena are even more pronounced in K_2O-containing glasses, as Fig. 42 shows. In Fig. 43, a more complex correlation of the $\log O_2$ concentration vs the composition ratio in some borate glasses is given. These data may be compared with the publication by A. Paul and R. W. Douglas[53] and the theory of borochromate groups like $[O_3 - Cr - O - B(O_{\frac{1}{2}})_2]$ (cf. Vol. VII. ¶ 694).

[50] *Phys. Chem. Glasses* **6**, (6), 197–202; (1965); **7**, (6), 209–210 (1966); and the interesting discussion notes by A. P. Herring, and by S. M. Budd, *ibid.* **7**, (6), 210–213 (1966); a reply by Nath, Paul, and Douglas, *ibid.* **7**, (6), 213–215 (1966).

[51] *Glass Ind.* **47**, (5), 252–256, 279, 281 (1966); see also *Bull. Amer. Ceram. Soc.* **47**, (3), 294–297 (1968).

[52] *Bull. Centr. Glass Ceram. Res. Inst. (Calcutta)* **13**, (3), 83 (1966); **13**, (4), 94–101 (1966).

[53] *Phys. Chem. Glasses*, **8**, (4), 151–159 (1967).

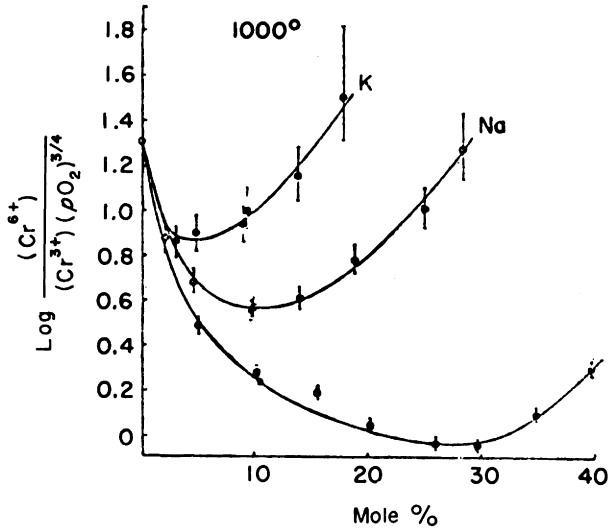


FIG. 42. Effects of nature and concentration of alkali oxides on the $Cr^{3+} \rightleftharpoons Cr^{6+}$ equilibrium in binary alkali borate glasses at 1000°C in air. (Nath.)

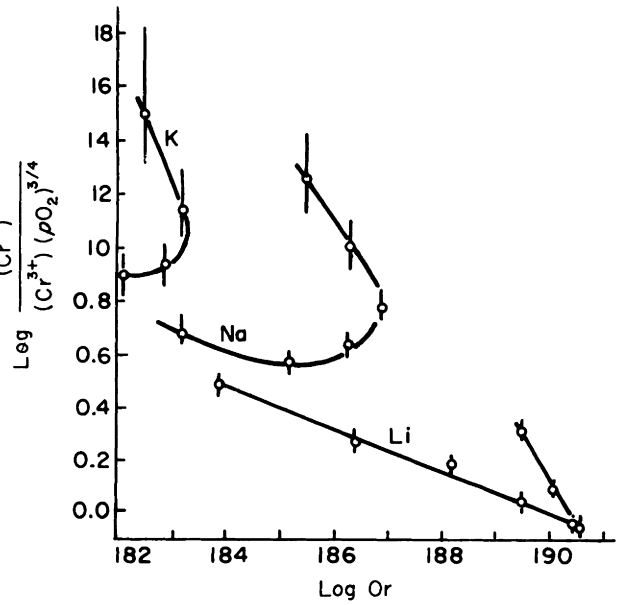


FIG. 43. Relationship between $(Cr^{3+})^{\frac{3}{4}}/(Cr^{3+})(p_{O2})^{\frac{3}{4}}$, and log total oxygen in binary liquid borates at 1000°C. (Nath.)

141. J. Kocík,[54] in the same manner as Knupp and Berger (see ¶ 139) observed for Cr and Fe, gave an extensive description of the optical determination of variant color effects, and measurements of the extinction coefficients as a function of the wavelengths, when $KMnO_4$ and $K_2Cr_2O_7$ combined were added to the batches of a normal Na–Ca silicate glass. The rather complex transmittance curves are reproduced in optical density curves in Fig. 44 in eight steps of $K_2Cr_2O_7$ additions from 0 to 2.0 mole %, and with constant 0.5% $KMnO_4$, with violet, dark-brown to black colors, as suitable for the purposes of infrared photography.

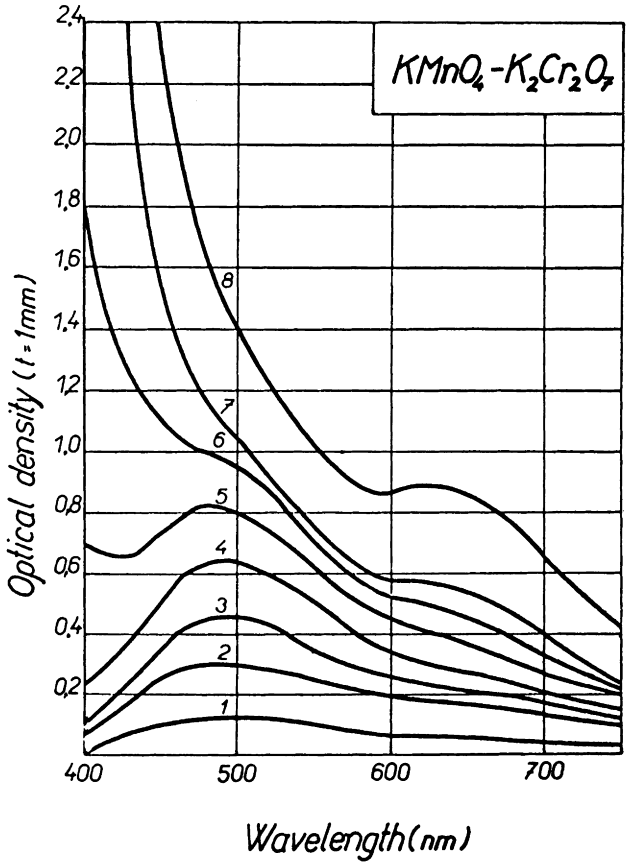


FIG. 44. Optical density vs. wavelength for eight different glasses (basic composition $1.5Na_2O$; $0.5CaO$; $6SiO_2$), colored by $KMnO_4$, and with variable addition of 0 to 2.0% $K_2Cr_2O_7$, by weight. (Kocík.)

[54] Vetro Silicati **9**, (6), (54), 9–11 (1966); *Proc. Int. Congr. Glass, June/July 1965; Sect. I*, 1, 111, pp. 1–7.

142. Which influences are exerted by the combustion gas atmospheres of glass furnaces were examined by L. Penberthy and G. Freeman,[55] especially on ultraviolet-absorbing green glasses while keeping the introduction of Fe from batch contaminants and incidental corrosion of refractory linings of the tank furnace at a minimum, but under furnace atmospheres changing from strongly oxidizing to neutral, and again to strongly reducing conditions. The oxidizing fusion conditions favor green glass with a high absorption in the ultraviolet, but a high transmittance in the infrared. When the atmosphere is modified to a neutral and then a reducing state, the spectrophotometry over a range from 350 to 800 mμ shows all the changes as discussed above.

143. Pairwise interactions of different coloring cations were again studied by A. Paul and R. W. Douglas[56] for the influence of Fe and Mn "contaminating" additions to Cr-green glasses. Characteristic pairs are Cr – Fe, Cr – Mn, Cr – As, Cr – Ce, and Cr – Mn – As, using optical absorption spectrophotometry and chemical analysis methods combined, for the quantitative controls. As a rule, the mutual interactions of such pairs are not essentially different from the oxidation–reduction titration practice well known from aqueous solutions. There are also no indications which might speak for the formation of complex compounds. From changes in the equilibrium constants as a function of the temperature, and the experimental determination of those constants derived from redox oxides, the enthalpies of the reactions involved, and their combinations, were calculated. There is an elementary additivity of those single enthalpies. In this respect it is important to note very good agreement of the experimental results with the redox tables established long ago by W. A. Weyl, Cl. Kühl, and H. Rudolph,[57] and those of H. J. Tress.[58]

144. Very interesting color effects have been observed in glasses containing *titanium* and *vanadium*. Among these we find results of investigations by W. Jahn[59] on Ti-violet colored phosphate glasses, in strikingly variable intensities of different hues; they have low refractive indices, combined with a high optical dispersion ν. The color intensities are a direct function of the content in Ti^{3+}; exchange of Na^+ in the glass matrix by K^+, or of Mg^{2+} by Ba^{2+} brightens the color. When the ratio of the alkali ions R^+/P^5 is above 1.2, the glasses become colorless; the violet color appears restricted to ratios below 1.2. Deep-violet to black and opaque glasses correspond to specific resonance effects in the ratio Ti^{3+}/Ti^{4+}. Such glasses have a very

[55] Symp. Colored Glass, Int. Comm. Glass, Prague, 1967, pp. 251–262.
[56] *Phys. Chem. Glasses*, **7**, (1), 1–13 (1966).
[57] *Sprechsaal* **71**, 91–93 (1938); **71**, 104–108 (1938); **71**, 117–118 (1938).
[58] *Phys. Chem. Glasses* **1**, 196–197 (1960); cf. ¶ 126.
[59] *Glastech. Ber.* **39**, (3), 118–126 (1966).

short fusion characteristic, and cannot be reproduced easily. Decolorization effects are dependent on the degree of change from $Ti^{3+} \rightarrow Ti^{4+}$, caused by addition of As_2O_5 or Na_3AsO_4 to the glass batch. The colored glasses do not show any phototropic reversibility in daylight and darkness. In the easy transition from one to another valence state, the Ti-colored phosphate glasses are in many respects similar to those containing Mn as a coloring agent.[60] On crystalline Mn–Ti phosphates, e.g., $NaTi_2(PO_4)_3$ see Ref.[61]

145. Studies were made by W. D. Johnston[62] of the optical properties of *vanadium*-containing Na silicate glasses (e.g., Na_2O, $2SiO_2$) which are equally determined by the conditions of variable oxygen partial pressures in the furnace atmosphere. The three-, four-, or five-valent V appears in these glasses compared in their individually very characteristic absorption spectra over the range $\lambda = 250$ to 2000 mμ to crystalline V compounds, e.g., those described by G. J. Kakabadse and E. Vassiliou[63] (cf. Fig. 45). The crystal-field theoretical treatment of the spectroscopic data proved to be in favor of the electronic configuration of the V ions, including the vanadyl ion $(VO)^{2+}$.[64] A special investigation of V^{5+} ions in binary alkali borate glasses and their

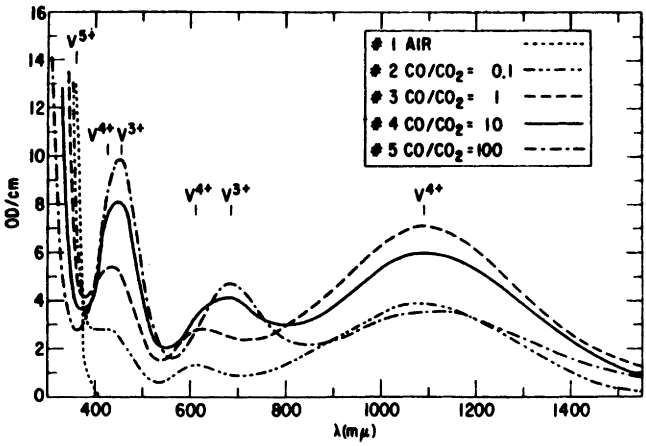


FIG. 45. Optical density/cm vs. wavelength for samples of vanadium in Na_2O, $2SiO_2$ composition glass prepared at various oxygen partial pressures. (Johnston.)

[60] Cf. H. Lux and E. Fröschel, Z. Anorg. Chem. **257**, 59–66 (1948).

[61] Yu. K. Delimarskiĭ V. N. Andreeva, and T. N. Kaptsova, Kopovidi Nauk Ukrainsk. SSR, pp. 492–494 (1962); W. Götz and R. Niebergall, *Naturwissenschaften* **56**, (1), 75 (1969).

[62] J. Amer. Ceram. Soc. **48**, (12), 608–611 (1965).

[63] *Phys. Chem. Glasses*, **6**, (2), 33–37 (1965).

[64] Cf. C. K. Jörgensen's ligand field studies, *Acta Chim. Scandin.* **11**, 73–85 (1957); specifically on V glasses also C. J. Ballhausen and H. B. Gray, *Inogr. Chem.* **1**, 111–122 (1962).

ultraviolet absorption spectra in the range of 220 to 310 mμ by A. Paul and J. M. Rusin[65] teaches a certain analogy with aqueous buffered solutions over the pH range from 2.5 to 12.5, as a function of the ratio R_2O/B_2O_3, and in the range of pH from 7 to 8, with the transition of $[VO_4]^{3-} \rightarrow [VO_3(OH)]^{2-}$. A certain analogy exists also in the structure unit for both types, namely, the glasses of the configuration $[VO_4]^{3-}$ and $[VO_3O_{\frac{1}{2}}]^{2-}$, with a bridging oxygen anion (cf. Fig. 46). Highly characteristic of these conditions is the appearance of a distinct "hump" area in the spectra from 225 to 295 mμ (corresponding to $\nu = 44.44$ to 33.90×10^3 cm^{-1}). Tentatively it may be suggested to formulate borovanadate complexes with structural groups of the type

$$\left[O_3V-O-B\begin{matrix}O-\\O-\end{matrix}\right]^{2-}$$

in equilibrium with vanadate and diborate anions: $(VO_4)^{3-}$ and $(B_2O_5)^{2-}$.

146. Spectrophotometric measurements combined with magnetic studies, made by A. Abou El-Azm and A. M. A. Nassar[66] disclosed the structure of V-containing Pb borate and silicate glasses. When the PbO/B_2O_3 ratio was higher than 3, Pb^{2+} ions are sited in interstices of the glass framework, and are not framework-forming cations, with a reduced number of ionic bonds. When PbO was replaced by alkalies or alkaline earth oxides a slight change in the molecular extinction effect ϵ and the mass susceptibility χ was observed which is attributed to a change in the screening of the V atoms. When the polarizability, *i.e.*, is decreased, the basicity of the glass melt favors higher valences of V and the formation of vanadates, thus explaining the high diamagnetic susceptibility of those glasses. For Pb silicate glasses, the parameters ϵ and χ are higher than those determined in Pb borate glasses, indicating that the interspaces in the silicate glass frameworks are distinctly more rigid.

147. In respect to the high importance of *cerium*-containing glasses, and generally of glasses containing other rare-earth elements in their application by the modern electronic industry,[67] the investigations by A. Paul and R. W. Douglas[68] have a particular significance for the equilibrium $Ce^{3+} \rightleftharpoons Ce^{4+}$ in binary alkali borate and silicate glasses (type $3Na_2O \cdot 7SiO_2$; $3R_2O \cdot 7B_2O_3$; $2R_2O \cdot 8B_2O_3$), to which const. 0.5 wt. % Ce had been added. The glasses were melted in Pt crucibles at 1100° and 1400°C, respectively. The quenched glasses in which the three- and four-valent Ce

[65] *J. Amer. Ceram. Soc.* **52**, (12), 657–660 (1969).

[66] *Centr. Glass Ceram. Inst. (Calcutta) Bull.* **17**, (3), 88–95 (1970).

[67] See the very instructive publication by the Thorium Ltd., Major Extension, Glasses in Glass **45**, (12), 471–473 (1968).

[68] *Phys. Chem. Glasses* **6**. (6), 212–215(1965); discussion remarks by A. P. Herring and S. M. Budd, *ibid.* **7**, (6), 209–213 (1966), followed by an asnwer from Paul and Douglas, *ibid.* **7**, (6), 213–215 (1966).

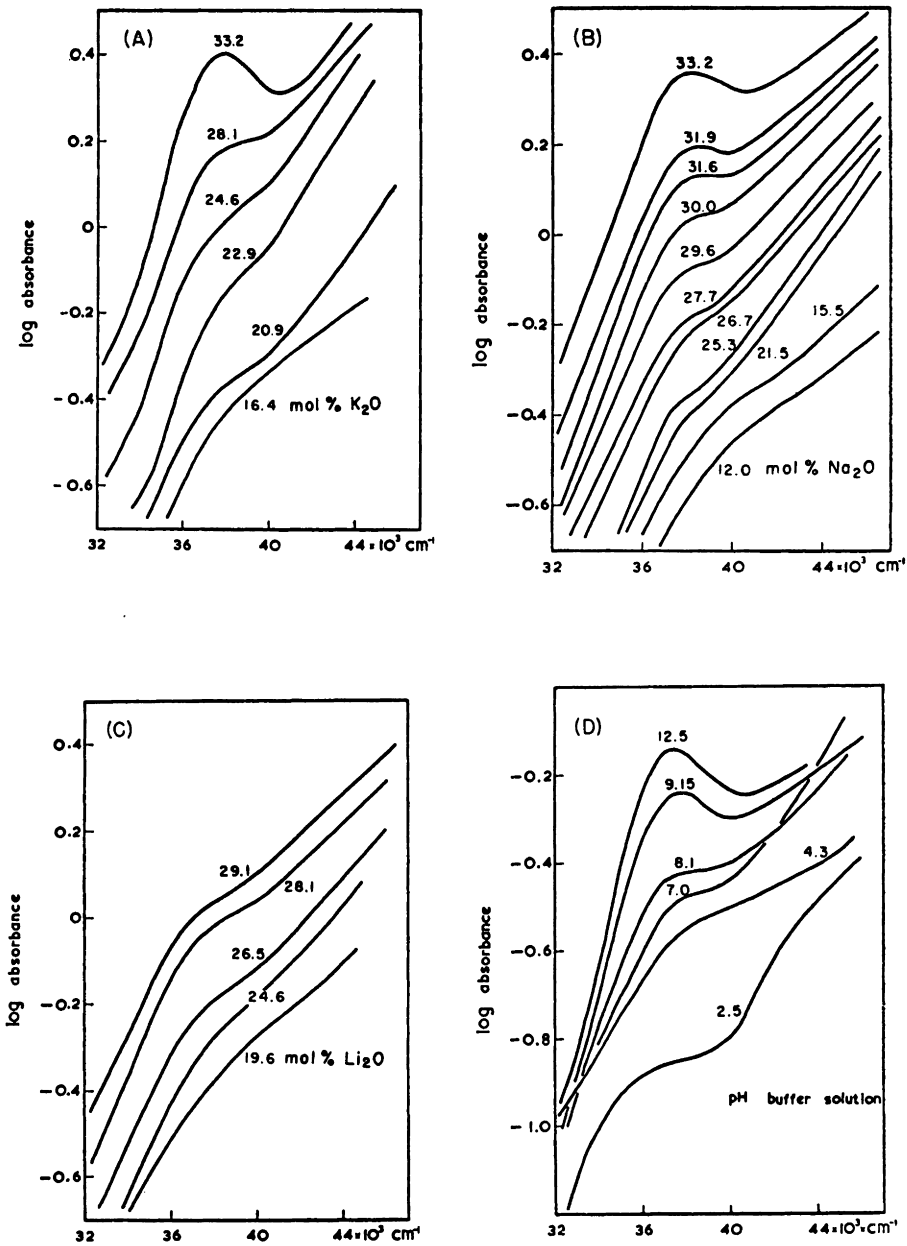


FIG. 46. Log absorbance vs. frequency curves of different alkali borate glasses, variable in mole percentage of R_2O contents. (A), (B), (C) for R = K, Na, and Li, respectively; (D) pH buffer solutions for comparison. (Paul and Rusin).

distribution was finally determined by chemical analysis, teaching again that Pt distinctly influences the equilibria of the additional oxides. As a rule, however, it is established that increasing concentrations in alkalies, or the transition from lithia to K_2O shifts the shares of Ce^{4+} in the resulting glasses. There is a linear correlation between $\log(Ce^{4+}/Ce^{3+})$ to the mole % R_2O; the shapes of the corresponding curves are nearly identical for the borate glasses (at 1000°C) and the silicate glasses (at 1400°C). The reaction enthalpies for $Ce^{3+} \rightleftharpoons Ce^{4+}$ could be derived; they increase with increasing glass basicity; the equilibria shift towards Ce^{4+} with increasing concentrations of Ce in the glasses up to 0.7%.

148. X-ray fluorescence of glasses containing rare-earth-elements was applied by E. Ramous[69] with best accuracy of the determination for Ce and Nd, as a decolorizing agent for Mn-stained glasses; it is satisfactory for the identification of other rare-earth elements, even those present only as "tracers." Presence of Fe does not disturb the analytical processing in any way. In this connection we appreciate also a special study by G. Paoletti and L. Tedesco[70] on controlled staining and decolorization of glasses by erbium. The color of Er-containing glasses is of a pinkish hue which is specifically characteristic of this rare-earth element ion. The decolorization in combination of Er with Nd is recommended as an excellent example of purely physical (additive) effects of this kind, with an optimum which is better than that of all the other decolorization agents developed earlier.

149. Concerning color effects of *copper*-containing glasses we wish to avoid here any repetition of what has been presented in Vol. VII. ¶ 46, 707–712, which deal with the Cu ruby glasses and their technological significance. We mention only the studies of A. Ram and S. N. Prasad.[71] Concerning the purely ionic colorization effects, the oxidation–reduction equilibrium in molten $Na_2O \cdot 2SiO_2$, in contact with Cu (and Ag) metal was investigated systematically by variation of the oxygen partial pressure above the melts. The equilibria

$$4Cu^{2+} + 2O^{2-} \rightleftharpoons 4Cu^{+} + O_2$$

and

$$4Cu^{+} + 2O^{2} \rightleftharpoons 4Cu^{0} + O_2$$

play the determining role here.[72] Interesting optical absorption studies were made

[69] *Vetro Silicati* **9**, (4), (52), 5–8 (1965).

[70] *Vetro Silicati* **11**, (3), (63), 13–15 (1967).

[71] *Centr. Glass Ceram. Res. Inst. (Calcutta) Bull.* **13**, (4), 85–89 (1966); for the role of *tin* in the striking of Cu ruby glasses, see the same authors, with K. P. Srivastava, and S. N. Prasad, *Trans. Indian Ceram. Soc.* **29**, (2), 35–40 (1970); cf. Vol. VII. ¶ 46.

[72] Cf. W. D. Johnston and A. Chelko, *J. Amer. Ceram. Soc.* **49**, 1966 (10) 563.

by A. Paul[73] on *chloride*-ion-containing Na borate glass melts. These experimental conditions are the more interesting as very early[74] such comparisons had been made in the absorption spectrum in the visible range in the system $CoCl_2-HCl-H_2O$ for a comparison of chlorocomplexes, e.g., $[CuO_{(n-m)}\ Cl_m]^m$. The tendency for their evolution however, decreases with increasing basicity of the solvent. In Na borate glasses those complexes contain one chloride ligand per Cu(II) center. Analogous Cu(I) complexes appear in aqueous and chloride borate melt solutions, all the Cu(I) absorption bands being in the ultraviolet. In the infrared, the (λ = 800 mμ) band corresponds to the asymmetric [Cu(II)] transition, varying in intensity and shape with the introduction of chloride ligands into the melts. The electron spin resonance spectrum of the Cu(II) complex does not show any significant change due to the formation of a chlorocomplex in the borate glass, the Cu^{2+} ions being in tetragonally distorted octahedral sites. This fact strikingly contrasts with the properly "dramatic" changes of the ultraviolet spectra of the Cu(II) Na borate glasses (Fig. 47). It is regretted that there is no possibility here to discuss in an equal detail what A. Paul and R. W. Douglas[75] described as the chloride ligand reactions of Co(II) Ni(II) and Fe(III) in HCl-and $HClO_4$-containing Na borate glasses and solutions with corresponding changes from octahedral to tetrahedral symmetrical complexes. It may

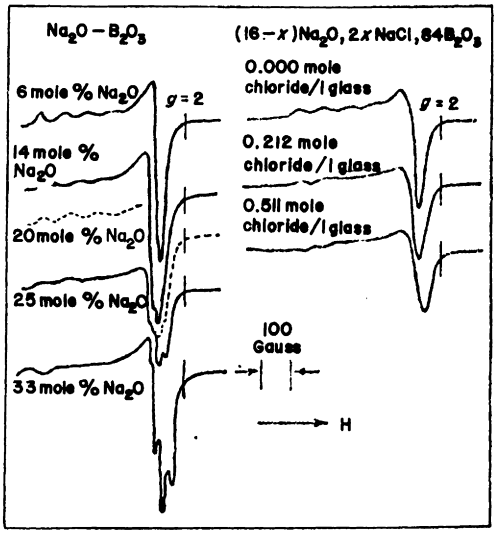


FIG. 47. Electron spin resonance spectra of copper(II) in sodium borate glasses. (Paul.)

[73] *Phys. Chem. Glasses*, **11** (5), 159–167 (1970).
[74] H. Pfeischifter, Ph.D. Thesis, Univ. of Berlin, 1937.
[75] *Phys. Chem. Glasses* **9**, (1), 21–26 (1968); **8**, (6), 233–237 (1967); **10**, (4), 133–137 (1969).

be that the activity of the alkali chloride in the melts is a considerable factor, e.g., also for the substitution of Cl^- ions by O^{2-} in the basic complexes.

COLOR CHANGES CAUSED BY IRRADIATION LUMINESCENCE

150. As a supplement to glass coloring systems we report in our text first a comprehensive article published by M. S. Aslanova and M. A. Yakovleva[76] on colored glass fibers (filaments), specifically for those electrical industries which use glasses on the basis of $CuO-CaO-MgO-Al_2O_3-SiO_2$ and $V_2O_5-CaO-MgO-Al_2O_3-SiO_2$. The melts had to be made in Pt crucibles; the filaments were spun from special nozzles and bushels in the laboratory, and semiindustrial scales, from 100 channels. Green-colored fibers could be manufactured from $CuO-Cu_2O$ additions up to 36 mole %, brown fibers from glasses with 8–11 mole % V_2O_5; above 13% V_2O_5 the glass became highly viscous and opalescent. The electric conductance of glasses with 18.6% CuO and 11.5% V_2O_5 are particularly suitable. It is interesting that the surface resistivity under the influence of atmospheric moisture causes an increase in the specific resistance in the measure that the water content increases, whereas in most of the other glasses the contrary effect is observed. The conductivity in the CuO colored glasses is simply ionic, in the V-colored glasses, a mixed electronic–ionic.

151. In the following, we have to consider multiple properties of industrially equally important glasses, and how they behave under the *impact of radiation* energies. Simple coating processes are often preferred to more sophisticated measures like the choice of rare-earth elements in the glass composition. From the rich experience of the Schott, Genossen, Mainz, Plants, and H. Schroeder[77] reported on methods for controlling the transmission of radiation through glass, first by application of very thin special coatings over larger areas with, or without, changes in the spectral intensity distribution—or for deliberately enacted reductions of infrared and ultraviolet shares in sunlight. One may also use light diffracting coatings of variable degrees of transparency. We must also consider here application of metal films, applied by volatilization and deposition of dielectric and semiconducting coatings with absorption and/or interference effects, and reflecting materials (cf. Vol. II.B. ¶ 157, 178) or lusters (cf. ¶ 130). New wyas have been found for "anchoring" Fe_2O_3 and TiO_2 coatings on the surface,[78] with Ti^{4+}-siloxane bonds. Such coatings make the glass surface acid and alkali resistant, including colored layers in

[76] *Sklář Keram.* **17**, (8), 250–251 (1967).

[77] *Glastech. Ber.* **39**, (3), 156–163 (1966).

[78] E.g., as brookite or anatase deposits, cf. H. Bach, *Naturwissenschaften* **51**, (1), 10–11 (1964).

which Co^{2+} and colloid-dispersed Au play a specific role, and may make the glass ultraviolet-impervious (when, e.g., TiO_2 is combined with Ce_2O_3). Similarly, glasses with selective reflection properties have been developed[79] to absorb solar radiation by a material of very low thermal emission, and by selective reflection-interference filters.

152. Under the impacts of *electron bombardment* of glow discharges in fluorescence tubes, the damage done inside these tubes was studied by Kl. Peter.[80]. Migration of Na^+ ions in the high electrostatic field in the surface layers[81] loosens the structure and makes Hg vapor enter the glass to a depth of about 60 μ (when the electrons are accelerated by 1 keV).[82] This process is accompanied by an intense *blackening* effect in the glass by incorporation of finest Hg droplets condensed in the loosened glass structure which can be made visible in electron micrographs (by plastic film replica techniques). In contrast to this phenomenon, a pure ultraviolet radiation is not able to cause any blackening of the glass tube walls or any cathode sputtering. Hg-free working fluorescence tubes do not show any color changes.

153. The problem of universally applicable glass *dosimeters* is in principle solved by an Mn – As pair-doped borate glass, developed by A. Bishai and S. Arafa,[83] when exposed to γ radiation (exposure intensities in the range from 10^4 to 10^7 rads). The color indication effect is based on the photochemical reaction of $Mn^{2+} \rightleftharpoons Mn^{3+}$, and a stable optical absorption band, induced by ionizing radiation of 515 mμ (2.42 eV). The low atomic numbers of the glass constituents make the dosimeter glass less dependent on the energy distribution of the γ radiation (cf. Vol. II.A. ¶ 359, 361).

154. P. Schleifer, M. Boczuch-Laczka, and Wł. Bazan[84] described photosensitive and photochromic glasses (compositions are tabulated), containing as active agents halogenides of Ag and Ag_2S, with light emission response and the appearance of a latent image. The photosensitivity process involved is *per se* irreversible, whereas typically photochromic glasses show reversible photochemical reactions (cf. Vol. II.B. ¶ 216).

155. Problems of *dosimetry for nuclear radiation* measurements (γ and neutrons emission) were studied again by W. Jahn[85] (cf. II.A. ¶ 359, 361). We mention this

[79] Cf. H. Schröder, *Glas Email Keramo Tech.* **17**, (5), 161–165 (1966) (cf. II. B. ¶ 158).

[80] *Glastech. Ber.* **40**, (5), 181–184 (1967).

[81] Cf. J. Rassow, Optik (Stuttgart), **33**, 382–389 (1966).

[82] Cf. J. L. Lineweaver, *J. Appl. Phys.* **34**, 1786–1791 (1963).

[83] *Bull. Amer. Ceram. Soc.* **46**, (11), 1102–1109 (1967).

[84] *Szklo Keram.* **19**, (12), 361–362 (1968).

[85] *Glastech. Ber.* **42**, (5), 176–182 (1969); s.a. Wissensch. *Tech.* Veröffentl. Glaswerk Schott & Gen., Mainz, 1969/70, pp. 119–126.

report again only to emphasize the high practical importance of such an instrument for detection and control in nuclear plants, especially for detection of threshold intensities transgression. The special glass developed for such aims (type PBG 11) is of borophosphate compostion, and determined for the range from 5×10^4 to 1.6×10^7 rad (γ = 510 mμ), with a saturation limit of about 10^9 rad. B-free special glasses for reactors, as so-called film detectors, and for personnel protection, and other photoluminescent types for neutron dosimetry are on the basis of Ca *meta*-phosphate, and fission-track methods. For more on K–Pb silicate glasses with luminescence response, see C. Bettinali, V. Gottardi, and B. Locardi.[86]

156. Concerning color centers in X-irradiated Na silicate glasses we recall to the reader's mind the excellent investigations by H. L. Smith and A. J. Cohen,[87] simultaneously under the action of oxidizing and reducing conditions, and with particular emphasis given to the rare-earth cations Ce^{4+}, Eu^{3+}, and Yb^{3+} (cf. Vol II.A. ¶ 364 f.388). The same may be concerning thermoluminescence phenomena for glasses with color centers in alkali silicate glasses, according to C. Bettinali, G. Ferraesso, and G. Bonetti.[88] In addition, a highly valuable bibliography on the application of the luminescence methods for determining the constitution of glasses was presented by C. Bettinali, V. Gottardi, and G. Ferraresso,[89] with very instructive schematic figures, showing the grouping of absorption bands on irradiated silicate glasses, their glow curve types, thermoluminescence and fluorescence spectra, a classification of the color centers (Fig. 48), and the application of the thermoluminescence model for Na aluminosilicate glasses in Fig. 49.

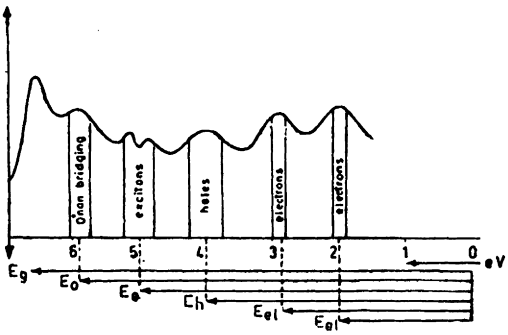


FIG. 48. Absorption bands of irradiated silicate glasses. (Bettinali, Gottardi, and Ferraresso.)

[86] *J. Noncryst. Solids*, (1), 360–370 (1969) (cf. II.A. ¶ 362).
[87] *J. Amer. Ceram. Soc.* **47**, (11), 564–570 (1964).
[88] *Vetro Silicati* **9**, (6), (54), 5–8 (1965).
[89] *Vetro Silicati* **10**, (3), (57), 5–12 (1966).

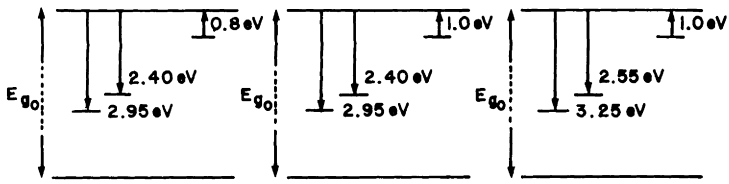


FIG. 49. Thermoluminescence model proposed for Na_2O-SiO_2 and $Na_2O-Al_2O_3-SiO_2$ glasses. (Bettinali, Gottardi, and Ferraresso.)

157. Thermoluminescence in highly pure synthetic silica glasses was studied by S. Cohen (cf. Vol. II.A. ¶ 358; Vol. V.B. ¶ 211).[90] These glasses, doped with Al, were under the action of different kinds and intensities of irradiation (X-ray, γ-ray, accelerated neutrons in oxidizing and reducing atmospheres), γ-induced absorption bands in K borate glasses, doped with Ce^{4+}, Bi^{3+}, Pb^{2+}, and Tl^{+} were discussed by A. M. Bishay and M. C. Maklad.[91]

158. A. J. Dudek[92] demonstrated how intensive bubbling in glass and its melts can be provoked by high energy electron bombardment with impacts of 80 and 145 keV, as observed in the scanning electron microscope, an observation which was often made by practical exposure of glass material with an evolution of oxygen gas,[93] combined with damage done to the homogeneity of working glass, and brown staining.[94]

159. A more recent publication by H. J. Dudek[95] described the serious damage done to plate glass surfaces by focused electron irradiation which is not only a thermal phenomenon but discloses effects of charge transfer. When the glass surface is, before irradiation, covered with a thin layer of conducting carbon, no Lichtenberg patterns appear on the glass but, under the action of a current density of about 80 $\mu A/mm^2$ more or less ellipsoidal cavities are engraved in an irregular distribution. An increased current density produces more extensive flat pits. This characteristic phenomenon is best explained by an evolution of space charge clouds like those described by M. P. Borom and R. E. Hanneman.[96] Oxygen which is formed by the

[90] *Vetro Silicati* **11**, (1), (61), 13–16 (1967).

[91] *J. Amer. Ceram. Soc.* **50**, (10), 503–508 (1967).

[92] *Glastech. Ber.* **41**, (1), 10–12 (1968).

[93] So-called Lineweaver effect, cf. J. L. Lineweaver, *J. Appl. Phys.* **34**, 1786–1791 (1963).

[94] See also gas eruptions after delayed boiling in the surface of glass; cf. A. J. Dudek, *Naturwissenschaften* **57**, (9), 450 (1970).

[95] *Glastech. Ber.* **451**, (5), 10–13 (1972).

[96] *J. Appl. Phys.* **38**, (5), 249 f. (1967).

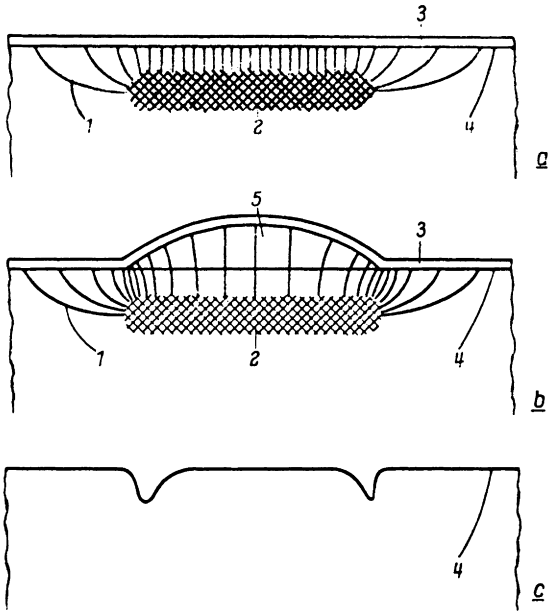


FIG. 50. Evolution of surface structures of glass. (1) field lines; (2) space charges; (3) carbon cover coat; (4) effective glass surface; (5) accumulation of oxygen gas. (Dudek.)

chemical interaction of the charge cloud with the glass-surface substance may break through a thin bloated glass skin into the vacuum. There is even marginal *sintering* of the decomposed glass grooves under the local action as steep temperature gradients develop, up to the transformation range of the glass (compare the evolution of such processes as shown in Fig. 50). This destroys the original glass structure and makes it porous over distinct domains.

160. Photoconducting Cd borosilicate glasses have been developed by V. Čáslavská, D. W. Strickler, and R. Roy[97] which, however, tend to unmixing and metastable crystallization.[98] In corresponding *germanate glasses*, the photo response improves to an optimum, whereas TiO_2, V_2O_5, MnO, MnO_2, Fe_2O_3, Cu_2O, NiO, PbO, and Bi_2O_3 strongly deteriorate and even may entirely suppress the photoconductance effect (cf. II.A. ¶ 358).

161. A very particular role amidst the staining elements introduced in normal, and special glass compositions is that of *selenium*; not only in respect to the colors of selenides of heavy elements, but also for the important *decolorization* processes

[97] *J. Amer. Ceram. Soc.* **52**, (3), 154–157 (1969).
[98] Cf. *J. Mater. Sci.* **3**, 440–445 (1968).

for which Se is of great industrial significance. In the recent literature on this subject not only the so-called colloid-dispersed theory of Se colors has been intensely discussed (I.C. ¶ 93 Vol. II.B. ¶ 54, footnotes 60, 71.). The origin of very undesirable Se losses in the process of ruby glass production[99] and the general behavior of Se in the batch fusion reactions, and their kinetics also have been studied. M. Boffé, C. Dupont, and G. Letocart[100] widely applied differential-thermal and -gravimetric analysis methods for this purpose, along with visual and spectrophotometric observation of changes in color intensities and spectral shifts, as a functicn of Se added to batches containing Na_2SO_4 and $NaNO_3$. It was generally concluded that the behavior of Se and of its compounds during the batch reactions is independent of the manner in which the Se is introduced, but that in every case the first Se compound formed in the batch mixes is Na_2SeO_4. A partial substitution of Na_2CO_3 by Na_2SO_4 is unfavorable since SO_2 and SO_3 evolved in the gas atmosphere reduces selenates and selenites, thus promoting Se losses by volatilization either as Se vapor, or as SeO_2 from the melts. On the other hand, additions of $NaNO_3$ to the batch promote the formation of selenates which are much more sluggish in decomposition reactions.

162. The optical properties and the well-known non linear absorption of CdSe in glass were studied by A. M. Bondh-Bruevich, T. K. Razumova, and G. M. Rubanova.[101] The establishment of a pronounced absorption edge is interpreted as the result of indirect mutual transitions between the bands of microcrystallites of CdSe, whereas the properly non linear transmission of the CdSe glass cooperates with the empty holes in the conduction band of the electronic configuration, in the non linear type of the conduction model.

163. The high requirements which modern electronic glass industry postulates for the qualities of special glasses make a strictly critical study, e.g., of the common lead silicate and borosilicate glasses indispensable. A very impressive example[102] for this fact may be seen in the publication by R. S. Barker, E. A. G. McConkey, and D. A. Richardson concerning the X-irradiation effects observed in the optical absorption characteristics of lead silicate glasses. Two absorption bands at 2.36 and 3.31 eV of maximum intensity (Fig. 51) show in their coloration and fading characteristics the type $\log N = k(\log(t + c) + b)$, with N the number of electrons trapped on defects (to develop color centers). The variation with the dosis of irradiation for the two Gaussian-shaped absorption bands consists of a superimposition of a saturation curve to a linear portion. For a given dosis the induced coloration

[99] Cf. Z. Karch, *Szklo Ceram.* **17**, (6), 144–149 (1966).
[100] *Sklar Keram* **17**, (8), 240–244 (1967).
[101] *Fiz. Tverd. Tela* **9**, (8), 2265–2273 (1967).
[102] *Phys. Chem. Glasses* **6**, (1), 24–29 1965; *Nature* **191**, (4786), 134 (1961).

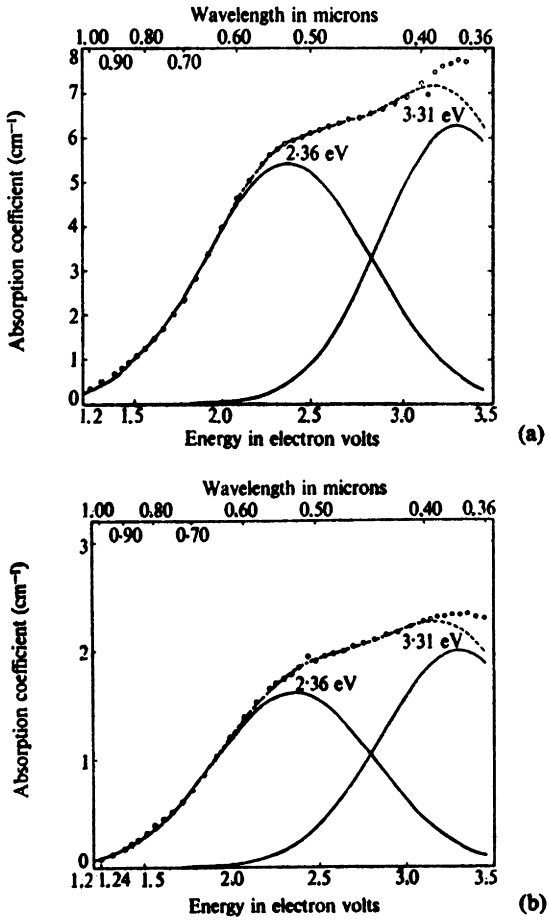


FIG. 51. Absorption spectrum induced by radiation. (Barker, McConkey, and Richardson.) (a) A dose of 6×10^7 rads (measured 42 minutes after cessation of radiation; (b) A dose of 3.2×10^4 rads (measured 33 minutes after cessation of irradiation).

(staining) effect is higher for a heat-treated glass than for an annealed sample, thus indicating the development of defects by the heat treatment.

164. The excellent strength properties of glass composites which we repeatedly emphasized in our text are of particularly great importance when they are combined with special absorption qualities, for *slow neutrons* for the manufacture of control rods in nuclear reactor operation. P. W. McMillan and B. P. Hodgson[103] investigated

[103] *Glass Technol.* **5**, (4), 142–149 (1964).

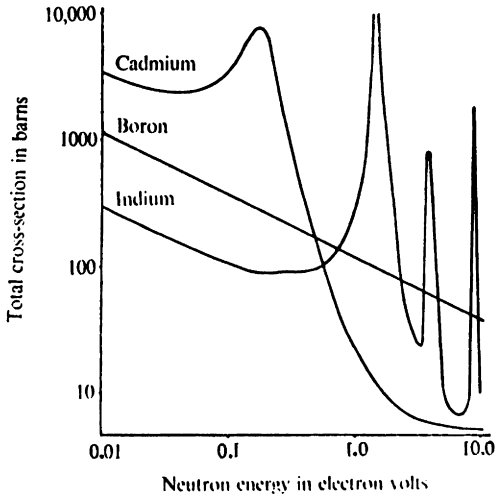


FIG. 52. Total slow neutron cross sections of cadmium, indium, and boron plotted from 0.01 to 10 eV. (McMillan and Hodgson.)

in this field special crystalline products from glasses of the systems $CdO-In_2O_3-SiO_2$ and $CdO-In_2O_3-B_2O_3$ with high captive cross sections for slow neutrons (cf. Fig. 52). These, however, made improved refractoriness desirable for achieving such rods by a controlled conversion to an optimum crystallinity, i.e., to Pyroceram-type products, a high thermal expansion coeffiient being no serious hindrance to the use of the rods encapsulated in steel. The Cd – In borate and silicate-type Pyroceram products are potentially useful for such applications, since they have a certain "reasonable" refractoriness, in addition to their high absorption for neutrons.

165. B. W. Garbrah and J. E. Whitley[104] demonstrate thermal neutron induced γ-irradiation methods for the rapid and reliable analytical determination of B in glass (in ranges from 1 to 7%). The neutron beam may best be taken from a reactor source with a multichannel analyzer, but possibilities for use of considerably simplified equipment for routine determinations are seen in a portable source and a single channel analyzer to count γ rays with energies between 425 and 550 keV.

166. The application of the classical O. Hahn emanation method (Vol. V.A. ¶ 95 f.) is commonly made for solid-state reactions, and have been discussed more in detail in Vol. V.A. The use of *inert gases* as radioactive tracers was demonstrated by Vl. Balek[105] for glass-technological purposes, when structural changes on the surface of batch reactants are in question, and for the study of phase inversions. Balek

[104] *Glass Technol.* **8**, (6), 154–156 (1967).
[105] *Silikaty* **13**, (1), 39–56 (1969).

solved this task by construction of equipment based on dynamic-thermal analysis and dilatometric measurements in combination with emanation-thermal measurements, e.g., for Fe_2O_3 or $CaSO_4$ as reactants, in the same meaning as typical solid-state reactions in studies of electronics ($BaTiO_3$ and ferrites) have been tested with remarkable success.

167. *Bismuth* (Bi_2O_3) -containing special glasses were investigated by A. M. Bishay and C. Maghrabi,[106] in binary and ternary mixes of the systems $Bi_2O_3-B_2O_3$ and $Bi_2O_3-Na_2O$. The infrared absorption spectra indicate the formation of $[BiO_3]$ structural units of the C_{3v} (Schoenflies) symmetry type and the introduction of nonbridging O atoms, whereas $[BO_4]$ coordination is enhanced by the presence of Bi (up to 45 mole % Bi_2O_3 in borate glasses, 25 mole % in the ternary Bi_2O_3–alkali borates). Very instructive is the comparison of the oxides Bi_2O_3, As_2O_3, Sb_2O_3 (the latter two in the crystalline state) and the changes by displacements of the peaks in the transmission vs frequency curves (Fig. 53). The formation of com-

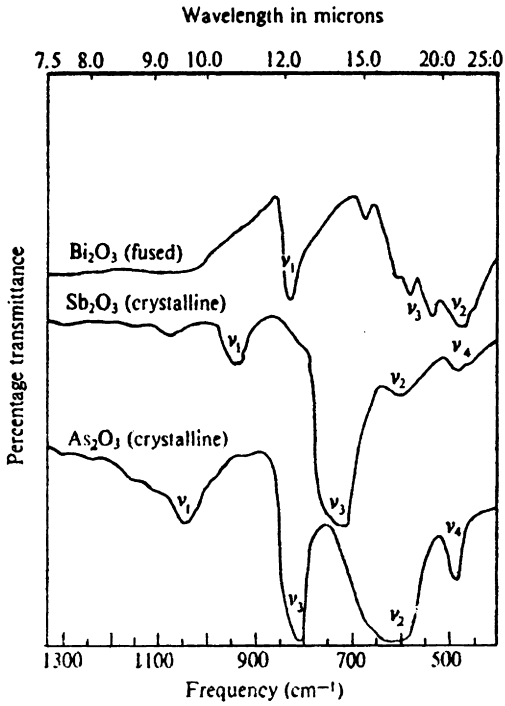


FIG. 53. Infrared transmittance of Bi_2O_3, compared with that of As_2O_3 and Sb_2O_3, using the KBr pellet technique. (Bishay and Maghrabi.) Note the displacement of the curves.

[106] *Phys. Chem. Glasses*, **10**, (1), 1–11 (1969).

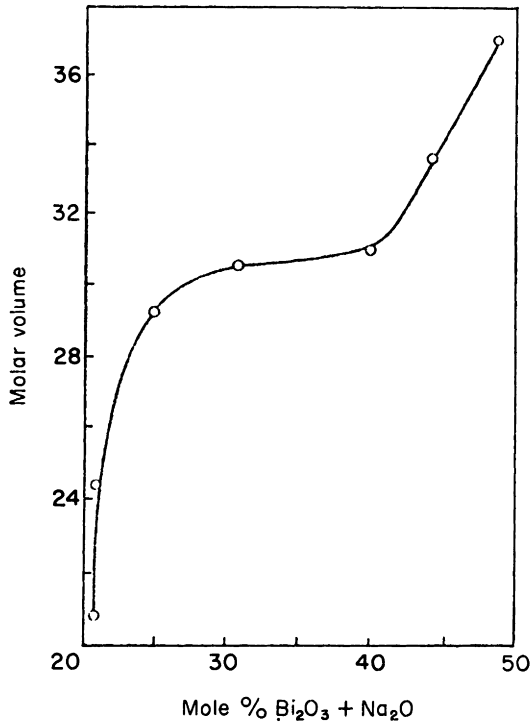


FIG. 54. Effect of Bi_2O_3 content on the molar volume of borosilicate glasses of type $1.0Na_2O$; $4.5B_2O_3$; xBi_2O_3. (Bishay and Maghrabi.)

pounds in the range from 37 to 53 mole % (Bi_2O_3 + Na_2O) is indicated by a large increase in the molar volume of the ternary glasses (Fig. 54). Such glasses have become of intense technological interest because of their analogies with corresponding lead-containing glasses. The two elements have nearly the same atomic weights and their ions Pb^{2+} and Bi^{3+} are isoelectronic.

MINOR HETEROGENEITIES; CORDS AND SURFACE-TENSION EFFECTS

168. M. Cable and C. Bower[107] spoke of "small-scale" homogeneity of laboratory melts, as commonly studied by measurements of light scattering in suspensions of glass powders in toluene or monochlorobenzene.[108] This method, however, cannot easily give really useful quantitative data on *local* enrichments, e.g., in CaO, which are very promptly determined by the microprobe.

[107] *Glass Technol.* **6**, (6), 197–205 (1965).
[108] Cf. the V. I. Shel'yubskiĭ method, Vol. II.B. ¶ 158.

The same problems of purely optical methods in the examination of heterogenities are extensively discussed by An. Winter, e.g., in her report 1966 on glass fining.[109]

169. J. Löffler[110] contributed to the complex problem from his newer experience with special work done by the International Commission of Glass,[111] L. Prod'homme[112] reported on advances of the fundamental principles of light diffusion in slightly heterogeneous glass.

On the origin of typically "physical cords," e.g., in pure silica glass, one may study interesting discussions by C. Tribuno and N. Tettamanzi,[113] with tentative interpretations on the basis of L. W. Tilton's "Vitron" theory of glass constitution.[114]

170. To conclude our discussion on glass heterogeneities we may add some publications the contents of which will later be analyzed.[115] W. Thiele[116] reported on new principles in the construction of cords detectors and measurement devices. S. C. Rademaker and H. J. de Rouw[117] also described beyond the interferometrically identified cord textures, defects caused by crystallization of cristobalite, corundum, or baddeleyite (ZrO_2), as characteristic segregations in striae which identifies their origin as either from batch residues or as corrosion products of refractory materials, or as "chemical heterogeneities" in glass melts, derived from volatilization losses which must locally change the glass composition.

171. M. Coenen[118] studied the density and flow characteristics of the heterogeneous cord glasses in using a buoyancy (Archimedes) method[119] to discriminate between the influences of variable compositions of cords and that of the matrix glass, e.g., for a Na–Ca silicate glass as the matrix, and amorphous alumina-enriched cord susbstance. In such composites it is not practically possible to draw reliable conclusions concerning the constitutional changes of the same materials at temperatures near the fusion limit, chiefly because of the variable convection factors and because constitution changes continuously with the coordination transitions $[AlO_4] \rightleftharpoons [AlO_6]$ as a function of the alkali content (ratio Al/R^+).

[109] Symp. on Defects in Glass, Tokyo–Kyoto, Sept. 1966, Contrbtn. No. 9, pp. 87–107; see also *Verres Refract.* **21** (3), 191–195 (1967) (6), 509–514 (1967); **22** (1) (1968) for photometric methods, cf. Vol. II.B. ¶ 35 and Phys. Chem. Glass, **9**, (5) 66A (1968), abstr. No./546.

[110] *Glastech. Ber.* **38**, (7), 269–276 (1965).

[111] Cf. *Verres Refract.* **19**, (4/5), 259–268 (1965).

[112] *Rev. Opt. Theor. Instrum.* **45**, (4), 163–176 (1966).

[113] *Verres Refract.* **21**, (4), 289–294 (1967).

[114] Cf. Vol. II.A. ¶ 209 ff.; Vol. VII. ¶ 392.

[115] Cf. 191, 484, 516, 531.

[116] *Z-Nachrichten*, (2), 75–100 (1958).

[117] Silicates ind. **28**, (12), 541–544 (1963).

[118] *Glastech. Ber.* **39**, (3), 81–89 (1966).

[119] Cf. VIII, II. 490.

172. H. Becker[120] investigated alumina-enriched cords in plate glass between 1000° and 1200°C and the mechanism of diffusion with the tendency for a composition of the heterogeneities by self-diffusion on one hand and cord material diffusion on the other hand. Confusion of these two intrinsically different mechanisms must bring about numerous errors in calculation of the material transport for a slow-levelling out of composition differences in systems as surprisingly complex as cords in glasses.

173. Always, when viscous flow factors interfere in the glass baths of tank furnaces cord glass conditions are observed and must be carefully taken into account as H. Becker did so well by the description of characteristic micrographs.[121] The viscous flow and the withdrawing mechanisms promoted by the flow, accelerate the diffusion rate under the tension gradients from the surface of the striae activating the phase boundaries. For these reasons, an accurate examination of the surface-tension distribution conditions in such elementary processes are of the greatest significance, e.g., for a theory of the Fourcault glass drawing method. Of course, we cannot analyze these highly fascinating technological problems in detail, but Becker's excellent report presented fundamental examples of how the entire range of problems may be successfully challenged.

174. The paramount significance of *surface-tension effects* (H. and G. Jebsen-Marwedel called them "dynactivity" phenomena) in such highly viscous systems as glass melts and porcelain glazes are in parallel fundamental properties of different products of organic chemical industry, like *varnishes*. This general experience was repeatedly emphasized in the excellent books by H. Jebsen-Marwedel on glass-technological defects, and on boundary face (interfacial) energies as impelling forces in the late fining and shaping processes in glass manufacture. The general importance of the principles of dynactivity applies to varnishes and related organic liquid products, with which a fascinating publication by G. Marwedel deals.[122] Varnishes correspond in a high degree to glass melts in density, viscosity, and surface-tension characteristics. It is interesting to see how much two branches of chemical technology apparently so far apart may learn from one another as is the case here. On dynactivity in varnishes with honeycomb textures as an excellent example for effects of boundary surface energy forces, see again H. Jebsen-Marwedel.[123] On dynactive material transport by varnish flow with a mingling of density, viscosity, surface

[120] *Glastech. Ber.* **39**, (12), 511–524 (1966).

[121] *Glastech. Ber.* **40**, (4), 124–136 (1967).

[122] *Farbe und Lack 69*, (6) 437–451; (1963), (7) 516–527.

[123] *Deut. Farben Z.*, (11), 435–438 (1960); report to Fraunhofer-Gesellschaft, München, 1960, Nov. 11, with a valuable color plate.

tension, and diffusion factors,[124] also Jebsen-Marwedel's proposals for terminology, and phenomenological classification.[125]

175. We may concentrate our attention on a few special methods for studying surface energy effects, among which the *radioactive tracer* method is one of particularly important help for the solution of many technological problems, indeed. For the glass industry, and also for the industry of hydraulic binders, C. Deschamps[126] indicated methods for control of glass in its surface level in a tank furnace; for surveying the thickness of refractory linings; for the formation of encrustations on the refractory brickwork of rotary kilns; for the detection of charge dislocation in vertical shaft furnaces, and the like, among typical everyday tasks of plant operation. Particular attention should be given to so-called *activation* of primarily nonradioactive tracer substances by application of neutron bombardment. For glass heterogeneity studies, commonly are used radioactive tracers like ^{24}Na, ^{89}Sr, and ^{32}P, whereas primarily inactive Ta and Ir are recommended after activation for direct controls. Another example is the determination of weight losses during service from ball mill grinders, traced with a radioactive isotope, and ensuing measurement of the radioactivity of the ground material—and many other daily tasks for surveying glass flow and diffusion,[127] and for base exchange measurements and control of chemical durability. On the control of glass flow as such we gave some information in Vol. II.B. (¶ 43 ff.) to which we may refer for a literature discussion by G. Steinke,[128] and some supplemental remarks in the following paragraphs.[129]

RHEOLOGY OF GLASS IN THE WORKABILITY RANGE

176. A general practice in *hydrodynamic investigations* may be adapted to glass technological studies of *glass flow* properties, and to develop suitable *model* systems and devices to *mix* glasses of different composition to homogeneity. A. R. Cooper, M. Cable, and I. T. Bradford[130] give a very instructive example with the use of glycerol as the "model liquid," in the place of molten glass. The electrical conductance of this substitute can easily be varied by adding a solvent, it promptly takes up a staining indicator like methylene blue, allowing study of striae (cords) and their

[124] Farbe u. Lack **67**, May, 276–293 (1961).
[125] Chem. Z. **30**, (12), 393–402 (1966).
[126] *Verres Refract.* **18**, (6), 467–473 (1964); see also Footnote[146]
[127] Cf. Vol. II.A. ¶ 90 ff. and, Vol. II.B. ¶ 75.
[128] *Sprechsaal* **99**, 329–339 (1966).
[129] Cf. ¶ 104. ff., on details of the application of the radioactive tracea methods.
[130] *Glass Technol.* **8**, (2), 48–54 (1967).

flow characteristics, to investigate the (three-dimensional) flow curves in large containers (these may be glass tanks or crucibles). Details of the homogenization process can be successfully observed when the heterogeneous liquid mix is stirred (the experiment showed that rotating discs are better efficient for homogenization than are simple rod stirrers). In all these ways, a numerical calculation of the hydrodynamic phenomena and their variables is possible.

177. The fact that many electric furnaces used to melt glass bring about to the foreground many specific problems which are different from conditions presented by the common flame-heating principle, is seen from ¶ 111, in the experiments of J. Staněk, L. Šašek, and H. Meissnerová.[131] In view of the hydrodynamic investigations necessary to control the flow of glass melts in an electrically heated furnace, new model experiments have been discussed extensively by H. Tober[132] who borrowed from Staněk *et al.* the application of a 7 to 8% solution of lithium chloride in glycerol as the model liquid for basic furnace model operations (with the dimensional reduction scale of 1 to 6.6, and bath temperatures for the liquid system between 65°C for the hot spot source, 40°C for the tank bottom space). Tober used the principle of the so-called light intersection method, combined with solid particles suspended in the liquid as the indicators for the flow patterns, in the place of the usual principles of staining of cords in the flowing liquids. By using different colors in the illumination of the suspended particles it was relatively easy to reconstruct, as a function of time, the three-dimensional flow curves from point to point (by small-scale camera photographs) in all essential details, for the control of the currents, variations in flow directions in space, and the rates of the flow.

178. Thus the important effects of the position of the electrodes for heating the system could also be accurately derived, including details of the influence of environmental conditions on the flow tendencies to and from the walls, the bottom, or the free surface of the bath. It may be sufficient here only to emphasize that energy distribution and flow patterns for the model concepts of electrically heated furnaces are in their deliberately simplified geometry, characteristically different from those in common flame-heated units. Nevertheless, the abundance of quantitative well-developed flow diagrams offer fundamental information of great value for the control of evolution and stability of the hot spot phenomena, and the establishment of thermal equilibrium in the entire unit. Among the many diagrams presented by Tober we only demonstrate here in Fig. 55 instructive flow patterns for a one-electrode pair model unit ("basic" model), and in Fig. 56 another one for a model of

[131] *Sprechsaal* **99**, 151–156 (1966); cf. ¶ 178 f., 181, 184 f., 189.
[132] *Glastech. Ber.* **45**, (2), 41–53 (1972).

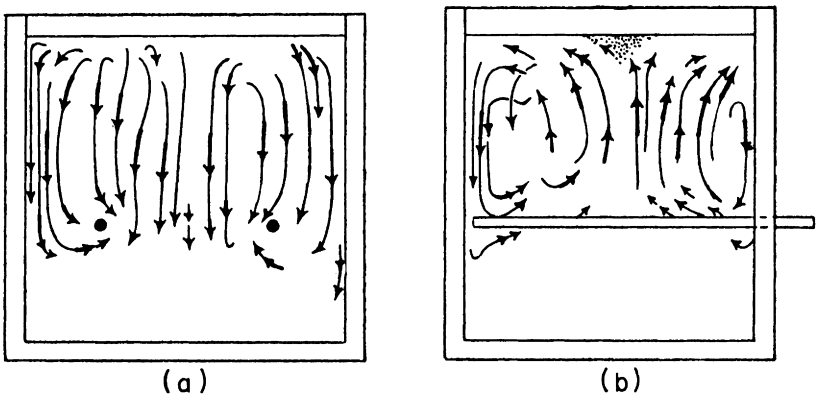


FIG. 55. Flow of molten glass currents in a model of a continuously working tank furnace. (Yober.) (a) section perpendicular to the electrodes on the front wall, in a depth of 3mm; (b) section through the center of the glass tank.

a tank with three pairs of electrodes, a throat heating, and one in the gathering end.

179 C. Bondy, J. P. Vidal, and G. Robin[133] (cf. Vol. II.B. ¶ 43, Footnote 51; Vol. VII ¶ 706) used activated tracers for an important example of the use of ^{182}Ta for accurate determinations of the stay period of glass melt in tank furnaces. We refer for this special case to the experiments made by B. Grislain[134] (cf. ¶ 106. ff.) and his observations of flow-homogenization problems of large melt bodies. On the other hand, G. Dusollier[135] studied by a tracer contact method the process and efficiency of welding processes, e.g., to determine a diffusion zone of Ca^{2+} ions for which a $\sqrt{t}$ time correlation in the growth of the layer thickness was established. Similar contact tracer methods were applied for the diffusion of Sn into the surface of a glass melt, and that of Cu or Ag into the Sn layer (of an order of magnitude of about 10 μ) (cf. Vol. VII ¶ 177, 540).

Among other interesting publications on the use of activated tracer methods for the flow of the glass in the tank furnace bath, we mention the following:

180. Pa. Ksiazek and Teresa Najbar[136] (cf. ¶ 105) used ^{24}Na from the technological viewpoint of a quality control of plate glass, by a possibly optimum maintenance of stable flow conditions. In a very similar way the same authors (with J. Byszewskiand Ma. Sura[137] extended the program of the first-mentioned investigation by application of different flat glass-drawing tanks, others for container and crystal glass kilns (one with crucibles), for a general comparison of their relative efficiency. As a numerical

[133] *Verres Refract.* **21**, (6), 524–529 (1967).
[134] *Verres Refract.* **21**, (6), 514–524 (1967).
[135] *Verres Refract.* **22**, (2), 163–169 (1968).
[136] *Szklo Ceram.* **18**, (33), (7), 202–205 (1967).
[137] *Silikattechnik*, **18**, (11), 345–349 (1967).

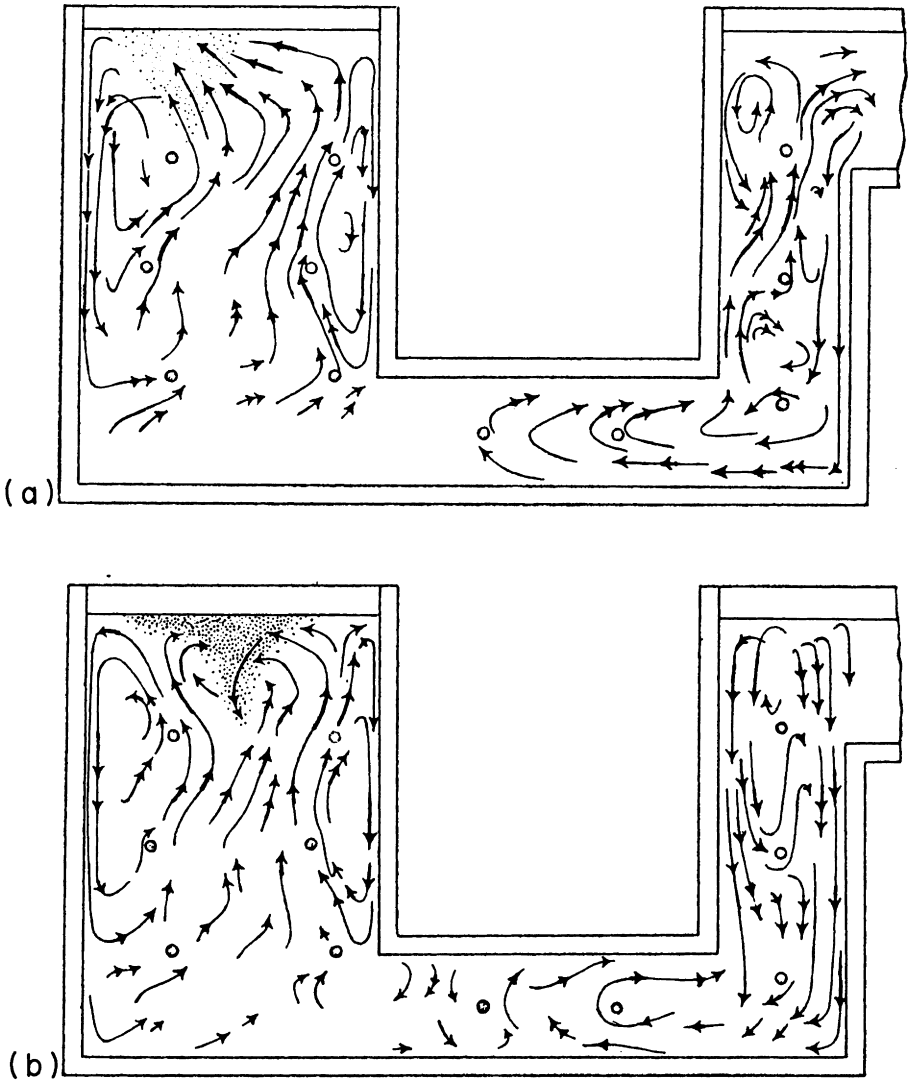


FIG. 56. Glass flow currents in a model of the continuous working glass tank furnace sections perpendicular to three planes of electrodes for heating. (Tober.) (a) Section through the center of the glass tank; (b) section in 10 mm from the front wall of the fusion tank, through throat opening and glass conditioner.

measure they chose the time period necessary for the doping radioactive tracer to appear for the first time in the product, i.e., after having passed with the glass flowing the entire length of the tank bath. In this way, it was confirmed anew that the glass flow, after an initial rapid gliding upon the surface layer, submerges into the bottom portion, then flows in helical curves towards the doghouse, a portion of the current being directed to the shaping (drawing) machines, the remaining melt being sub-

merged downward again, seized by the back flow, along the tank bottom towards the temperature maximum in the "hot spot" and in part returned into the withdrawal currents. Detailed measurements were studied of the flow speeds in the bottom and surface currents.

181. O. Zych, J. Pejtek, and O. Štepán[138] (cf. ¶ 108) who also worked in their glass flow studies with ^{24}Na, observed highly complex flow diagrams in the drawing chamber of the furnace (the machine was designed for shaping thick-walled glass tubes of large diameter), with phenomena of mutual superimposition, rather different flow conditions, and even back returns. The flow conditions of electrically heated glass tank furnaces were examined by J. Staněk, L. Šašek, and H. Meissnerova[139] (cf. ¶ 179) after a careful prestudy of a model flow medium. The Galilei and Grashof coefficients were accurately correlated to that of flowing glass in the tank furnace experiments, For this purpose a systematic adaption of the cinematic viscosity over the experimental ranges for both media, glass, and model liquid had to be made, including the electrical conductance (glycerol with LiCl solution). The flow patterns depend on the shapes of the flow curves, and are different for plate or rod electrodes. One may compare the different furnace and tank constructions with details of the conduction arrangement, from microfilm documentation of reactions in the melting-down batch pile to the events in the machine chamber, as they were described by D. D. Billings and W. A. Manring[140] (cf. ¶ 110). From the many technological details given in this report we mention only the comparison of tank constructions with transverse flame (so-called cross firing arrangement of the burners) and others with U-shaped (horseshoe) flame-heating systems.

182. In principle, the flow conditions of ceramic (porcelain) glaze melts are not essentially different from those for common homogeneous glasses melts. To picture these phenomena, M. Maultzsch and H. Scholze[141] used two efficient methods adapted to glazes for hard porcelains. In the first, the samples were exposed to reduction of SiO_2 in hydrogen to elementary Si (in a nitrogen–hydrogen atmosphere); Si as such is a strongly staining coloring agent. The second method used the common techniques of etching polished sections and examination under the interference microscope to evaluate regular etching profiles with both methods. The glaze melts showed the development of the same dynactivity characteristics as do "eddies" or cord-striae vortexes which are known from the numerous investigations of H. Jebsen-Marwedel *et al.*, for common glass in the surface portions during the firing process. In the glost-firing period of ceramics, i.e., of the glazed shard, one

[138] *Silikaty* **13**, (1), 67–73 (1969).
[139] *Glass Technol.* **10**, (2), 43–49 (1969).
[140] *Glass Ind.* **50**, (8), 382–386 (1969).
[141] *Glas Email Keramo Tech.* **20**, (1), 1–4 (1970).

liquid layer with a markedly higher surface tension overlaps another liquid layer with a lower surface tension, as is confirmed by very impressive interferometric micrographs taken after the etching experiment.

SURFACE REACTIONS OF FLOWING GLASS MELTS IN CONTACT WITH REFRACTORIES

183. In general, the technological reaction phenomena on the contact surfaces between glass melts and refractory wall materials are important enough for us to dedicate a special Chapter of our text to newer literature on those factors which determine the course and evolution of reactions and defects in glass tank operation.

H. Wermbter and H. Scholze[142] explained the specific corrosion effects observed on modern fusion-cast refractories (on Al_2O_3 basis, with addition of ZrO_2) and the changes of viscosity with the amounts of such oxides. Characteristic of the ternary system $Al_2O_3-ZrO_2-Na_2O$, CaO, SiO_2 (see Fig. 57) is the existence of quite distinct ranges of compositions for which the viscosity at a given temperature is minimum. Such better mobile melts must exert a strong influence on the corrosion behavior of the refractory material with the glass as is made evident by the abundant presence of dissolution cords clearly visible in cross sections through the resulting glass (molten in crucible tests).

184. J. Löffler[143] especially studied the development of the so called "flux joins" in the refractory lining, this time of typical alumina refractories (Monofrax, Corhart, and the like), with meniscus sculptures on these in consequence of corrosion directed by surface energies. The spreading phenomena evident here are often surprisingly similar to the well-known patterns which appear on the borders of tumblers filled with mixtures of alcohol and water (for microscopic studies and identification of minerals like nepheline, formed in the corrosion reaction zones to which we refer in ¶ 487 f., 491 which also deals with microscopic interferometric measurements.[144]

185. The well-known formation of so-called "upward drilling" pitting holes in refractories was extensively studied also by J. Löffler,[145] in analogy with the development of the flux joins in flat glass tanks. The essential result of these investigations is the description and explanation of a mechanism which Löffler called an alkali-"pumping" circulation of the melts *in situ* which causes a continuous flow exchange of fresh glass with the normal alkali content, onto the join surface to a three-phase

[142] *Glastech. Ber.* **43**, (8), 319–322 (1970).

[143] *Glastech. Ber.* **41**, (12), 513–522) (1968).

[144] See also previous measurements by H. J. Tress, *J. Soc. Glass Tech.* **38**, 89T–100T (1954).

[145] *Glastech. Ber.* **38**, (10), 398–405 (1965); **40**, (10), 374–378 (1967); **43**, (8), 329–330 (1970).

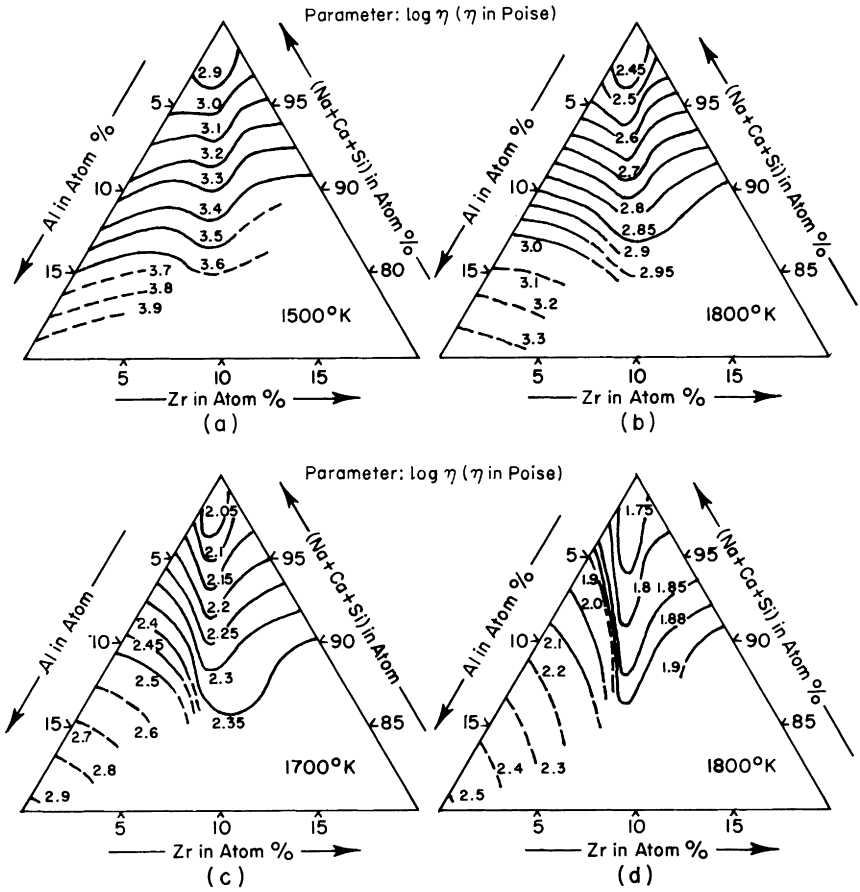


FIG. 57. Effects of alumina and zirconia of the temperature–viscosity parameters of Na – Ca silicate glass melts over the range from 1500° to 1800°. (Wermbter and Scholze.)

contact where in most common cases either a gas bubble, or a metal drop, comes into immediate contact with the refractory composite, to react chiefly with the alumina in it. This process can be studied very well by a highly similar model system with a liquid mixture of ethyl alcohol and water. Microscopic-interferometric examination of the dynactivity makes evident how the surface energies help, starting from small cracks in the surface of the solid (refractory) material to "catch" bubbles from the flowing liquid to come into circulation, and "pumping" effects starting from then on. This complex phenomenon may also extend to small metal droplets (of Pb or Ag) in the place of the bubbles, with, in principle, the same drilling hole end effect. An important premise is the presence of a *positive* meniscus being formed when liquid and refractory are in contact (Fig. 58).

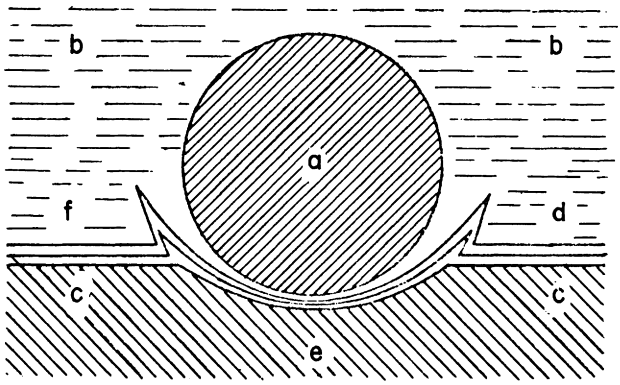


FIG. 58. Schematic representation of a silver sphere wetted by a glass melt prepared in a fireclay crucible, after a short reaction period. (Löffler.) (a) Silver sphere; (b) normal glass melt; (c) reaction layer of alkali alumino-silicate; (d) layer impoverished in alkali on fireclay substratum; (e) fireclay crucible substratum; (f) normal glass, from which alkali is lost to the refractory substratum.

186. On the classical action of mere surface energies, R. Brückner[146] presented a concise mathematical solution for the surface-tension-based consideration of boundary surface convection which may arise, in spite of relatively low differences in the reciprocal surface-tension parameters of flow convection. Brückner distinguishes between free convection (including density and thermal-gradient-determined convection), and *coercitive* (i.e., mass capacity) flow convection, for the particular ideal effect of three-phase boundaries (with more or less developed miscibility ranges, perhaps). Model experiments to illustrate the boundary-surface convections in striae diagrams are extensively used in the special part of this fundamentally analytical investigation of the upward drilling phenomenon in refractories. The full display of these considerations was then presented by Brückner in systematic publications on the material transfer on the surface of silicate and salt melts, combined with the kinetics of the action, e.g., of Na_2SO_4 from the batch, or in the fining operation, also in a SO_2-containing furnace atmosphere.[147] For the special problems in glass tank furnace operation see also another important publication of the same author[148] from which we take Fig. 59 for an illustration of the upward drilling process,

[146] Rep. Int. Constrctn. Silicate Conf., 2nd, Polytech. Inst. Architect. Buildg. Res., Weimar, 1966, pp. 54–77.

[147] Cf. *Glastech. Ber.* **34**, (11), 515–528 (1961); **35**, (2), 93–105; (1962); on the mechanisms and systematics of the elementary processes on boundary face convection see also Koll. Z. **222**, (1), 39–50 (1968).

[148] *Glastech. Ber.* **40**, (12), 451–462 (1967), with a rich reference bibliography.

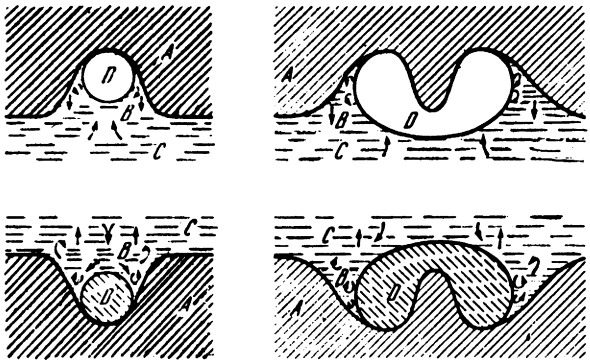


FIG. 59. Schematic representation of preferred corrosion by boundary face convection around gas bubbles or liquid drops. (Brückner.) (*A*) Refractory body; (*B*) Dissolution Product Melt; (*C*) Corrosive Melt; (*D*) Gas Bubble; (*D'*) Melt Drop, immiscible with Melt *C*).

with three-phase conditions of foreign gas bubble inclusions as the dynactive agent, and/or of metal droplets in corrosion grooves, initiating the evolution of "pins" or "taps" in the refractory block.

187. In all essential features, there is a good agreement between Brückner's observations and conclusions on the process of "upward drilling" and those established by T. S. Busby and J. Barker,[149] also with fascinating model experiments with methanol–water–ice, in the presence of gas bubbles. In details, the last-named authors distinguished a certain different behavior of smallest gas bubbles (of diameters between 0.1 and 0.5 mm) which undergo upward–downward directed dancing movements, and reach a relatively high rate in the drilling effects, whereas medium size bubbles (of 0.50 to 0.80 mm) move only on the lateral contact with the ice wall. All of the largest bubbles observed do not build up any regular corrosion profiles. A highly characteristic development of the flux lines described in those experiments is completely analogous to that in refractory block corrosion, thus confirming that upward drilling and flux line attack are manifestations of one and the same complex reaction in multiphase joins and contacts.[150] A more chemical process for about the same general situation of corrosion reactions, is defined in ideas of P. Hrma[151] in connection with the role of oxygen potentials on boundary surfaces, and diffusion

[149] *J. Amer. Ceram. Soc.* **49**, (8), 441–446 (1966).

[150] See also E. R. Begley and R. O. Herndon, *Amer. Ceram. Soc. Bull.* **49**, (3), 633–637 (1970), with demonstration of a direct correlation existing between "metal line" and "upward drilling" in many different specimens taken from industrial conditions, at different temperatures (correlation coefficient = 0.87).

[151] *Verres Refract.* **24**, (4/5), 166–168 (1970).

coefficients on contacts between glass and refractories which we discussed in VII ¶ 289. According to A. Pons and A. Parent[152] both factors are functions of activity.

188. A transfer from the phenomena of electrochemical corrosion of metals by aqueous solutions to analogous ones in the interaction of molten glass with different metals, is discussed in an interesting article by A. Parent.[153] Direct current intensity, and potential curves for such combinations were measured using a C. Deportes and M. Darcy[154] standard oxygen electrode in galvanic cells, with Na silicate melts as the electrolytes. Curves of coupled anodic–cathodic effects[155] were applied to control directly determined weight losses for the metals and their alloys, the corrosion of which could be currently observed under the heating metal microscope. It was thus possible to develop a qualitative classification of corrosion resistivity for certain groups of alloys which is, however, restricted to Cr-free compositions for the immersion cell conditions used by Parent in his high-temperature experiments with surface changes caused by the corrosion in silicate melts, and to construct the Tafel lines for the cathode–anode polarization. As a reversible reference electrode, stabilized zirconia proved optimum for the measurements at high temperatures. The depth of immersion of the metal samples into the glass melts is of great importance, influencing the quantitative results of such measurements. An essential factor is the formation of a true flux line (metal line) groove of the same type that is so common in glass tank linings, on the level of the phase discontinuity contacts glass melt/furnace atmosphere/refractory or metal.

189. In this connection, we may briefly return to the flux line phenomena and upward drilling (pitting corrosion) from the viewpoint of previous discussions by J. Löffler, on the action of molecular forces and transport effects connected with a continuous change of constitution of reaction glasses, as indicated in a higher corrosion efficiency, and the higher surface tension of the glass caused by the dissolution chiefly of alumina.

190. Evidently, not only the corrosion activity of the molten glass on the surface of refractory linings, for silica refractories specifically in the superstructure, must be taken into account. *Alkali vapors* from the volatilization source of the open liquid surface are also a factor of in no way negligible significance in practice. In this direction, investigations made by A. V. Morsanyi[156] (cf. ¶ 253) are highly instructive. He

[152] *Verres Refract.* **23**, (3), 324–333 (1969).

[153] *Verres Refract.* **23**, (3), 300–311 (1969); cf. Vol. II.A. ¶ 177.

[154] *Silicates Ind.* **26**, (11), 499–504 (1961).

[155] Method of J. M. Defranoux, see *Bull. Soc. Fr. Elec.* (VII) **8**, 173–181 (1958); (VIII) **1**, (1), 672 ff. (1960).

[156] *Glass Technol.* **7**, (6), 193–196 (1966); **7**, (6), 196–201 (1966).

studied the behavior of different Na salts (preferably Na_2SO_4 and Na_2CO_3) volatilized from the glass surface and from batch dust under oxidizing, neutral, and reducing conditions at 1350°C. The Na_2SO_4 vapor is particularly highly reactive on the refractory wall material when the furnace atmosphere is reducing. The presence of water vapor promotes even this reactivity. In an oxidizing atmosphere, the action of Na_2SO_4 and Na_2CO_3 is smaller; the same is valid for NaCl, and particularly for Na vanadate. Presence of Na_2O in the corrosive vapors is indispensable; SO_2 alone, even in reducing atmosphere, does not bring about any corrosion on silica brickwork. On the other hand, extensive analytical determinations of the alkali distribution in the glass melt surface, and of alkali taken up by corrosion reaction onto the surface of the refractory in the superstructure demonstrate a certain limiting factor for the corrosion intensity, as a function of temperature when currently the alkali-containing reaction glass is withdrawn by a drain effect from the arch roof inner surface, and thus returns into the glass of the bath. This is the reason that one cannot use the alkali content of the surface reaction glasses of the slagged portions as a measure of the real wear deterioration intensity in the arch (cf. Vol. II.B. ¶ 104).[157]

191. The multiplicity of the arched roof (superstructure) interchange phenomena with the furnace atmosphere gives evidence of the significance of the corrosion problems with which the operation engineer must be familiar, and for which he must exert sufficient control for a constantly satisfactory glass production. This practical fact is the subject of investigations made by J. Daudans, A. Krings, and A. Sevin,[158] see Vol. II.B. ¶ 187, 203 for discussions of many details on the nature of cords and "stones" in glass, derived from refractory linings and the arched roof, most specifically also of the genesis of the so- called "nepheline worms" (¶ 499). R. Recasens, A. Sevin, and A. Gardiol[159] reported from a wealth of experience with different composition classes of glass, and different refractories used in tank furnace constructions, and on laboratory experiments of static and dynamic "dipping tests." Mostly, rods of the refractory samples were used for this purpose under, in principle, the same aspects as those in the work of Daudans *et al.*, to find empirical rules illustrating the resistivity behavior of both groups of materials, and a classification of the suitability of refractories from case to case, in contact with special glass compositions, e.g., the depths of the "metal line" grooves as measured on rods used for dipping controls (cf. Vols. II.B. ¶ 104; Vols. II.C ¶ 19 ff.; Vols. VIII. ¶ 188).

[157] See also the very instructive report by N. A. Shmeleva and L. F. Ivanova, *Steklo Keram.* **23**, (3/4), 184–187 (1966) [Eng. transl.: abstr, *Glastech. Ber.* **41**, (2), 73 (1968)] on the effects of the furnace atmosphere on the service life of fireclay refractories in pot furnaces.

[158] *Glastech. Ber.* **42**, (10), 391–395 (1969).

[159] *Verres Refract.* **23**, (1), 19–27 (1969).

PROBLEMS OF CONTACTS OF GLASS MELTS WITH GAS PHASES AND THEIR RELEASE

192. Again, one of the important merits of H. Jebsen-Marwedel in his investigations in glass technology research is his early recognition of the necessity of deeper based studies not only of fining problems, but of fining and after-treatment of the glass melts as soon as they leave the bridge chamber of the tank furnace. In one of his older publications[160] he underlined the significance of recognizing the temperature for an equilibrium of the gas content of the liquid bath as the signal for the end of the fining process. It is certainly understood that the practical operation of the glass manufacturing production requirements cannot afford to wait until theoretical (thermodynamic) equilibria are established. The engineer will therefore, try to end the "ripening" of the glass melt to the shaping process, to increase the temperature above the normal level at the right time for the gas content of the melts to reach a reasonable mode which does not affect a critical postulate of a desirable and permanent homogeneity, as it would be finally achieved when the real equilibrium would be verified. Very instructive experiments of Jebsen-Marwedel and Dinger made it clear that this is a possibility which, indeed, can be practically fulfilled. But there is a long way to go before practice alone will empirically find this way in every case. For this reason it is advisable to study the newer literature to learn how far most recent experience is in agreement with the conclusions and recommendations presented by technological experimentation.

193. The first step in this eminently practical problem is a systematic study of the gas content in the final state of chemical *dis*equilibria, relative to the theoretical numerical data of *gas solubility in glass* as a function of temperature, pressure, and glass composition. This purely empirical task calls for international cooperation of professional laboratories and organizations. It is remarkable how much the literature in this field extends in every direction. As an example of many, we may note the remarkable success of a Russian school of investigators who published a very rich experience with gasses in glass, and their analytical control. We enumerate valuable papers by V. T. Slavyanskiĭ which are collected in his book[161] on the spontaneous evolution of gas bubbles, e.g., in optical glass (with E. N. Krestnikova and S. A. Starodubtseva), and many more. M. Boffé, G. Letocart, M. Pierre, and E. Plumat[162] reported on the physical-chemical state of *vacuum melting* of glass, an industrial scale

[160] With K. Dinger, *Verres Refract.* **1**, (1), 19–25 (1947).

[161] "Gases in Glass," Gosud. Izd. Obor.-ov Promyshl. Moscow, 1957; many single reports in, e.g., *Steklo Keram.* **14**, (2), 1–7 (1957); **23**, (11/12), 579–583 (1966); or *Tr. Gos. Opt. Inst.* **24**, 293–309 (1957).

[162] Adv. Glass Technol., Tech. Paps., Int. Congr. Glass, 6th, Washington, D.C. 1962, pp. 52–74.

in order to improve and to accelerate the fusion period, although the vacuum furnace brings about increased effects of volatilazation from the surface of the melt, not to speak of difficulties arising from the introduction of the batch ingredients in a rather fine-granular form, and of using as raw materials oxides as glass constituents, in place of cheaper and easier handled natural minerals, rocks, and industrial products in the form of carbonates, nitrates, or sulfates. For mass production, the vacuum fusion process is not yet better accessible, although for the production of certain high-quality special glasses, e.g., glasses with rare metals and earths, for the very specific electronic purposes, the situation is much more favorable for electric-heated vacuum units.[163]

194. Very respectable advances, indeed, have been made for the control of the gas content in the form of *bubble inclusions* which are often of great importance for the full-understanding of the physical-chemical reactions from the batch, over the fusion period, to the state of the mature end product, before it is shaped. We mention here progress made in the gas analysis by application of *gas chromatography*, e.g., in the publications by K. H. Schier and W. Bauer,[164] the results of which were later disclosed by the authors, with S. Breitfelder.[165] The chromatographic method is based on the use of the β-ionization detector. The separation of the gases is made in the well-known columns filed with 20% dioctyl phthalate on a Sterchamol support (for the separation of SO_2 and CO_2 from N_2, O_2, H_2, and CO, the latter two gases absorbed on molecular sieve zeolites type 5 A, and 13 X). This method works with a sensitivity of 0.01 μl for N_2, O_2, and CO_2, but only 0.1 μl for SO_2.

195. A much more sophisticated gas-chromatographic apparatus for the analysis of bubble gases in glass is that more recently developed by H. Mairlot and P. Gilard[166] in which the gases were analyzed in one operation. To maintain a satisfactory degree of sensitivity in this method, the stability of the power supply for an electronic detector cell must be closely controlled, and the same is valid for amplifier devices coupled with the cell. Carrier gas used must be of highest purity (e.g., better than 99.99% He) when sensitive Wheatstone bridge wiring circuits are used to control the separation effects by thermal conductance measurements for the indicator systems. The detector system used by Mairlot and Gilard is a Gow-Mac type 9285 D cell with four Wo wires mounted as in a Wheatstone bridge in pairs of two separate chambers of the cell, one of these merely serving as a reference at the time when the gas arrives

[163] On recent observations on the vacuum fusion of glass see also M. A. Matveev in the book "Vitreous Systems and Materials." pp. 77–85, Izdat. Zinatne, Riga, 1966.

[164] *Silikattechnik* **14**, (4), 119–121 (1963).

[165] *Silikattechnik* **15**, 276–280 (1964).

[166] *Glass Technol.* **8**, (5), 123–126 (1967).

in the other chamber. The signal of the cell is amplified by a microvoltmeter (Hewlett-Packard 425 A). In the apparatus used by Mairlot and Gilard two columns for separation are provided, one filled with 10% di-2-ethylhexyl sebacate on Chromosorb W, working at room temperature, the second a 5 A molecular sieve column operating at 100°C.

196. *Mass spectrometry* is also one of the methods of predilection for gas analyses from bubbles in glass, as J. C. Neerman and F. R. Bryan[167] demonstrated, that is sensitive and accurate for bubbles down to 0.05 μl atom.[168]

P. Emer[169] studied the secondary evolution of gas bubbles in amber glass (cf. ¶93) after the fining was ended, using in this case a *stirring* of the melts to judge different degrees of tendencies to develop secondary foaming (cf. Vol. II. B. ¶81 ff.), with SO_2 and CO_2 as the principal gases. The experimental results in laboratory tests were in full agreement with industrial manufacturing on a small scale after making some applied corrections. This experience also agress with recommendations made by K.-H. Schier, W. Bauer, and W. Müller,[170] in this case with a glass for tube manufacturing. The characteristic gases in the bubbles were again N_2 and H_2 (in the percent ratio 15:85), in analogy with the fascinating problem of the role which N_2 may play in the solution state in silicate glasses in general (cf. ¶ 209 ff., H. O. Mulfinger *et al.* 1963, ¶ 273). For the study of such phenomena the temperature gradient furnace recommended by H. Jebsen-Marwedel and K. Dinger (see ¶ 192) is an important and accurate instrument.

197. Problems of the production of alkali-free glasses (with less than 10, sometimes even less that 2 ppm R_2O) on the basis of Pb – Zn or Al borosilicate compositions, as determined for electronic purposes, melted in electric furnaces, with a minimum of volatilization losses, have been overcome by using extremely purified raw materials, and keeping a very strict control of the low-pressure atmosphere in the furnace, which operates at 1500° to 1600°C.[171]

198. On the other hand, and in connection with early work by H. Möttig and W. Weyl,[172] K. Manikantan Nair, W. B. White, and R. Roy[173] gave evidence of what a high concentration of O_2 one may introduce into the glass melts under high

[167] *Anal. Chem.* **31**, (4), 532–535 (1959).

[168] See also a comparison with gas chromatographic determinations, by the same authors, *Anal. Chem.* **34**, (2), 278–280 (1962).

[169] *Glastech. Ber.* **37**, (1), 59–69 (1964).

[170] *Silikattechnik* **16**, (5), 158–159 (1965).

[171] Cf. B. Sunners and B. Narken, *Amer. Ceram. Soc. Bull.* **44**, (8), 620–622 (1965).

[172] *Glastech. Ber.* **11**, (2), 67–70 (1933).

[173] *J. Amer. Ceram. Soc.* **48**, (1), 52 (1965).

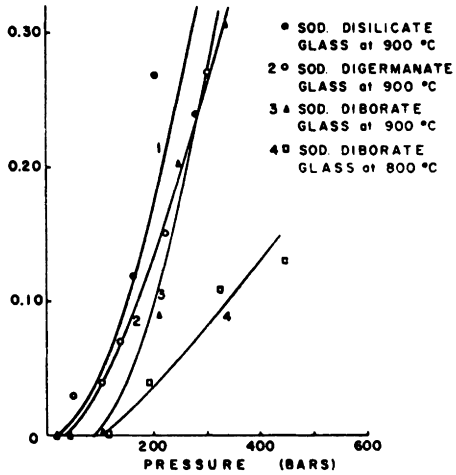


FIG. 60. Solubility of oxygen in different glasses as a function of the oxygen pressure. (Nair, White, and Roy.)

pressures, for given glass compositions (cf. Fig. 60), using a quenching technique as applied earlier by W. B. White and R. Roy;[174] for the spontaneous bubbling and foaming in "dry" and "moist" furnace atmosphere and for mixed alkali glasses, we refer to Vol. II.B. ¶ 73 ff., and articles by C. G. Rainer and M. C. Cable.[175] For the analysis of the gases in single glass bubbles A. R. Clarke and M. C. Cable[176] again used a special gas-chromatographic device filled with silica gel, and molecular sieve columns. The breaking up of the bubbles with a steel plunger made possible later determination of the individual diameters of single bubbles of voluming between 10^{-4} and 10^{-1} μl.

199. Just concerning the breaking-up process and the development of freshly broken glass surfaces, the adsorption behavior of gases on these was studied by R. K. Ware and P. P. Pirooz[177] who emphasize how this factor may introduce errors into the gas analysis of bubbles. Mass spectrometric measurements made it evident that CO_2 and SO_2 show adsorption amounts in the range of 0.02–0.05 μl/cm^2 of the fracture surface. Nitrogen and hydrogen are not adsorbed notably, O_2 only in subordinate amounts.

[174] *J. Amer. Ceram. Soc.* **47**, (5), 242–249 (1964).
[175] *J. Amer. Ceram. Soc.* **49**, (10), 568–571 (1966); **50**, (10), 528–531 (1967).
[176] *Glass Technol.* **8**, (3), 82–85 (1967).
[177] *Glass Technol.* **8**, (3), 86–87 (1967).

200. We have to emphasize in this connection[178] the importance of gas bubbles appearing in ceramic *glazes* (of hard feldspar *porcelain*) as described by A. C. Bersticker, H. J. Sweo, and J. D. Snow[179] for which a suitable gas extraction cell (with steel plungers for breaking-up the glass, of a typical biscuit glaze product) had been constructed. In this case, nitrogen prevails in filling the bubbles; oxygen is only minimal, evidently by a resorption in the glass melt. For the study of gas diffusion reactions as assumed here, the application of a deuterium-containing frit must be of particularly helpful service, also for an identification of real diffusion of gases into, and from the gas bubbles (cf. on the method recommended by F. Laves *et al.*, 1959/1960, cf. Vol. II.A. ¶ 120; Vol. II.B. ¶ 249 ff.) E. Galanulis and H. Scholze[180] treated glazed procelain bodies in the fritting state in an oxidizing, or neutral, or reducing atmosphere with a quenching of the bubbles for gas analysis of their content by mass spectroscopy. The principal gases were again N_2, O_2, CO, CO_2, and in low amounts also Ar, with particular conditions of adsorption for H_2O and CO_2 on the inner surface of the experimental container and on the fracture surfaces of glaze specimens. The O_2 content of the glaze bubbles distinctly increases with an increasing firing temperature. This fact is explained by the dissociation of Fe_2O_3 present in the body; but after a certain period, the amount of O_2 evolved into the bubbles again decreases, and N_2 increases, a phenomenon which is interpreted by the decomposition of chemically bound nitrides which typically occur in low amounts in feldspars as the raw material of porcelain bodies (cf. ¶ 212 f., 220) (Fig. 61).

201. Problems like those mentioned in ¶ 38 on the high-pressure synthesis of CO_2-saturated and over-saturated glasses (cf. Vol. IV.A. ¶ 199, footnote 321) are not only of geological and geochemical interest but were studied by D. M. Roy, S. P. Faile, and O. F. Tuttle[181] up to 10 kbar. The content of CO_2 and H_2O was determined by mass spectroscopy, that of Ar by X-ray fluorescence spectra from normal Na – Ca silicate, Na borate, and $K_2O,4SiO_2$ glasses (Fig. 62) for the gas-volumetric analysis data are in percents; the refractive indices of the glasses also were measured. For Ar the characteristic anomaly is that the increase in the refractive index, as a function of increasing hydrostatic pressure, is more rapid than would be expected as a mere effect of densification, evidently from the filling up of structural holes with

[178] As a useful bibliography of literature on the solubility of gases in glass in general, we recommend a publication (under this same title), by J. M. Fernandez Navarro and J. L. Oteo Mazo [*Bol. Soc. Espan. Ceram.* **7**, (2), 183–236 (1968), with 244 references].

[179] *Amer. Ceram. Soc. Bull.* **45**, (11), 1009–1011 (1966).

[180] *Ber. Deut. Keram. Ges.* **44**, (11), 533–539 (1967).

[181] In the book "Physical Chemistry of the Earth" (L. H. Ahrens, K. Rankama, F. Tress, and S. U. Runcorn, eds.), Vol. I, pp. 138 ff., Pergamon Press, New York 1958; and more recently *Phys. Chem. Glasses* **5**, 176–177 (1964).

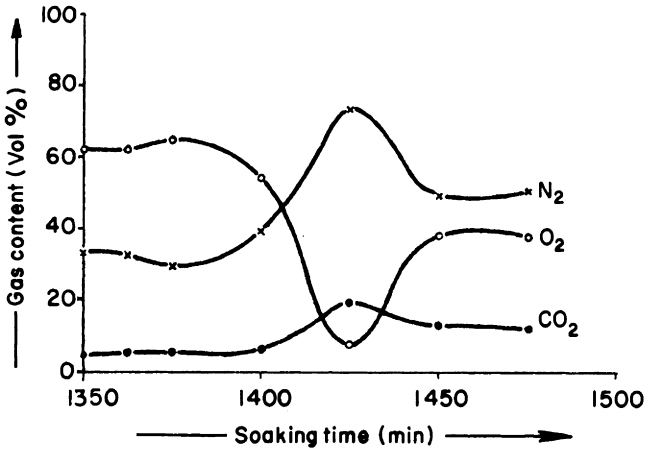


FIG. 61. Composition of gases included in glaze bubbles after firing in air at 1450°C as a function of soaking time. (Galanulis and Scholze.)

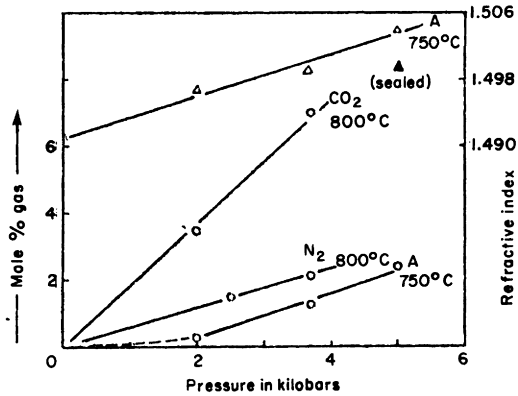


FIG. 62. Solubility of argon, nitrogen, and carbon dioxide in melts of K_2O, $4SiO_2$ as a function of pressure at selected temperatures. Upper curve shows refractive indices of the argon-containing glasses. (Roy, Faile, and Tuttle.)

the rare gas. In most cases, the gas-enriched glasses of this class are entirely homogeneous and do not show any bubbles in the electron replica micrographs.

202. Rich material from practical experience on multiple tendencies disclosed by refractory materials in contact with glass baths of tank furnaces was presented by L. E. J. Sainsbury,[182] combined with an extensive critical consideration of the

[182] *Glass Technol.* **8**, (6), 136–147 (1967).

applicability and reliability of so-called standard methods for testing given refractories in contact with liquid glass. It is possible only rarely to identify with satisfactory certainty the source of the bubbles during the industrial production in glass tanks. Bubbles definitely starting from refractories may be rather more the exception than the rule. The tendencies of different refractories to evolve bubbles are not necessarily reflected by and in the course of production.

203. H. Scholze[183] presented a valuable and comprehensive report on the appearance of gas bubbles in which he not only demonstrated that, in general, the physical solubility of different gases in glass melts is not relatively low, but that the "chemical" solubility by participation in heterogeneous gas reactions may become a much more decisive factor, specifically in respect with CO_2, H_2O, and N_2. This latter viewpoint is especially essential for reactions observed between nitrides (chiefly Si_3N_4) with oxygen, to evolve nitrogen *in statu nascendi* even when the "physical" solubility is low (cf. the important studies of H. Mulfinger, cf. ¶ 215 ff.). Analogous considerations were examined from the theoretical and practical viewpoints by H. Scholze and W. Lowsky[184] in porcelain *glazes* (cf. Vol. II.B. ¶ 229ff.), and E. Galanulis and H. Scholze.[185] "Pockiness" is another defect in the quality of porcelain articles (glazed or biscuit) caused by local bubbling, as was demonstrated by I. Berger.[186] The gas content of such "blisters" is commonly the same as it is in feldspar containing hard porcelains and glazes, namely, H_2O and N_2, but porcelains may be excessively rich in them when more than 25.5% water are sorbed in the raw body, or when grains of quartz have not been completely dissolved, or are not sufficiently fine milled. Newer experiments of I. Berger, however, contradict the latter conclusions; she is not of the opinion that nitrogen derived from nitrides primarily present in the feldspar is the true source of those bubbles, but assumes that the intermediate meta-kaolinite products of low-grade firing during its transition into Si-spinel[187] are that source.

204. I. Makino, Y. Murakami, and R. Yamagishi[188] give an impressive example of the application of the omegatron tube–Pirani gauge principles in mass spectrometry and qualitative or semiquantitative analysis of gases from bubbles included in glass when remaining as vacuum-melting residues. The species of fragment ions produced in the Omegatron are analyzed in normal mass spectroscopy. The

[183] *Ber. Deut. Keram. Ges.* **44**, (2), 59–63 (1967).
[184] *Keram. Z.* **20**, 777–778 (1968).
[185] *Ber. Deut. Keram. Ges.* **44**, (11), 522–539 (1967).
[186] *Silikattechnik* **19**, (1), 13–18 (1968).
[187] Cf. G. W. Brindley and M. Nakahira, cf. V. B. ¶ 68, 190 ff.
[188] Asahi *Garasu Kenkyu Hokoku* **19**, (2), 85–96 (1969).

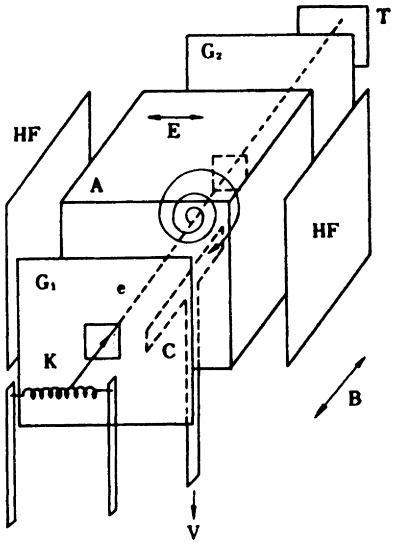


FIG. 63. Perspective sketch of Omegatron for gas analyses of glass inclusions. (Makino, Murakami, and Yamagishi.) B and E indicate the direction of magnetic induction and of the RF field. The spiral paths of ions are indicated; K is the cathode to emit the ionizing electron beams; HF and HF′ are electrodes to which the RF voltage is applied. C is an ion collector, V a connector to amplifier, G_1 and G_2 are grids, T a target.

minimum volumes which are accessible to the Omegatron method may be as low as 3×10^{-4} ml. The diameter of the bubbles may be more than 0.3 mm as shown for industrial plate glass and television tube glass (Fig. 63). The instrumentation for this method of mass spectrometry is best seen in previous descriptions by D. J. Todd.[189]

205. Classical problems involved with the apppearance of *amber colors* in glass (incidental or deliberately directed in glass technology) was again vividly discussed, mostly from highly practical viewpoints on the desirability, and limits of application, first theoretically by S. B. Holmquist[190] as a problem of thermodynamics and oxygen activity of SO_3 and SO_2 in silicate melts (cf. Vol. II.B. ¶ 21–26), then by a discussion of the influence of organic substance, e.g., the presence of C as such, or in organic compositions in glass sands as the raw materials, as presented by P. Wange, H.-J.

[189] *J. Soc. Glass Technol.* **40**, 32T–38T (1956); W. and S. Kruszewski, *ibid.* **38**, 65N–75N (1954), with older bibliography and references—and not to omit the older but still important publication by H. A. Shadduck and A. VanZee, *J. Amer. Ceram. Soc.* **25**, (3), 69–83 (1942).

[190] *J. Amer. Ceram. Soc.* **49**, (9), 467–473 (1966).

Blankenburg, and K.-H. Jagush[191] (cf. ¶ 112). For Na borosilicate glasses of Pyrex type, a brownish-yellow discoloration is highly undesirable. The authors made extensive spectrophotometric measurements of the transmissivity coefficients of such glasses in different states of the amber-color evolution, also as a function of their FeO/Fe_2O_3 content of the glass sands used, not only as a function of the content in humic acid substance. Different methods for the elimination of such agents were proposed to forestall the appearance of brown colors basically by fining with As_2O_3(+ $NaNO_3$) and the like (cf. Vol. II.B. ¶ 36).

206. Introduction of *sulfides* (chiefly CaS and MnS) from raw materials for the production of common houseware glass is easily accomplished when slags, chiefly *blast furnace slags*, are added to the glass batch for a cheap and rapidly melting aggregate as was demonstrated by R. Persson in an extensive examination of the problems involved.[192] In every case, an economical use of blast furnace slags (so-called "Calumite") for production of low-price glassware quality is possible, with some rules for safety, and even desirable because of a remarkable reduction of the fusion time from the batch, in comparison with the distinctly slower fusion processing of feldspar-containing batches.

207. Practical viewpoints for the use of amber glasses and the survey of them in containers of light-sensitive and high-quality beverages have been intensely discussed in the considering legislation for protection of consumers. An excellent example of the application of scientifically based tests in this field is the official Italian supervision of bottle production for wines and the like, which must meet carefully established specifications, especially for amber-colored containers.[193]

208. The constitution of the chromophore substance in *amber glasses* which is commonly identified with iron sulfides, was carefully investigated by R. W. Douglas and M. S. Zaman,[194] and then by M. S. Zaman and A. Paul[195] from a more technological viewpoint (cf. ¶ 113, 280). In the first-mentioned publication, the spectrophotometric and wet-analytical determinations of Fe^{2+} ions are carefully discussed. As a function of the concentrations in Fe(II) and Fe(III), and of the S^{2-} anion, the characteristic absorption at 425 mμ indicates the presence of a Fe(III) sulfide as the chromophoric principle proper. The extinction coefficient of the absorption at 425 mμ is, e.g., well observed in amber glass on the basis of the simple glass

[191] *Silikattechnik* **18**, (9), 282–285 (1967).

[192] Cf. *Glass Ind.* **47**, (10), 537–539 (1966); **47**, (10), 583–584 (1966). See also on CaS and MnS in slags, II.C. ¶ 12, 47 ff.

[193] Cf. V. Gottardi, *Ind. Agr.* **5**, (ott.) 551–554 (1967), and G. Paoletti, *Birra Malto* **14**, (7), 3–7 (1967), Rivista, with instructive spectrographic data, and literature references.

[194] *Phys. Chem. Glasses* **10**, (6), 125–132 (1969).

[195] *Glass Technol.* **10**, (4), 93–98 (1969).

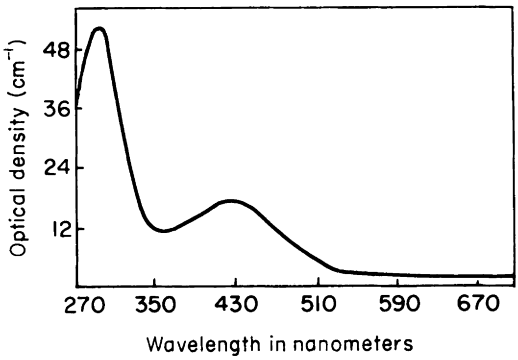


FIG. 64. Absorption spectrum of $3K_2O, 7SiO_2$ amber glass (iron addition 0.05 wt.%, estimated 0.125%). (Douglas and Zaman.)

$3K_2O \cdot 7SiO_2$ (Fig. 64), namely, 9,000 l cm^{-1} mol^{-1}; for a near-ultraviolet band at 295 mμ it is 26,000 l cm^{-1} mol^{-1}. By calculation from the intensities it is possible to distinguish between the shares in Fe^{3+}, surrounded by six O^{2-} anions, and those which are present in the chromophore, i.e., the share in the sulfide phase. Calculations also establish the equilibria in the amber glass between Fe^{2+} and Fe^{3+} cations, and SO_4^{2-} and S^{2-} anions separate in the matrix glass and in the chromophore. The second publication mentioned above refers to the development of a rapid physical-chemical method for the determination of the redox ions in the amber-brown glasses, as mentioned above, namely of Fe^{2+} by spectrophotometry in the well-known near-infrared line of $\lambda = 1\ \mu$, and analytical determination of Fe^{2+} and S^{2-} by titration with ICl. The total iron is titrated with thioglycolic acid, the total S by a special evolution method using Na hypophosphite for the reduction.[196]

INERT GASES DISSOLVED IN GLASS MELTS

209. The use of gas chromatography and mass spectrometry for the detection of minor amounts of the so-called inert rare gases, also in a wider meaning of *nitrogen*, is a field of applied physical chemistry which made great progress in the last decade, particularly in respect to investigations on the solubility and diffusion of such gases in silicate melts (cf. Vol. IV.A. ¶ 18ff.). H. O. Mulfinger and H. Scholze[197] investigated the behavior of helium, over a temperature range from 1200° to 1480°C, and under

[196] Similar to the method recommended by B. Philip and H. Dautzenberg, *Anal. Chem. Acta* **30**, 384 ff. (1964).

[197] *Glastech. Ber.* **35**, (11), 466–478 (1962).

1 atm pressure, with a solubility of 2.2 to 4.5 $\times 10^{-3}/cm^3$ of the glass (on the methods applied see the report of the same authors and H. Franz[198]). The glasses used in these experiments were common Na – Ca and Na – Ca – Al silicate glasses; with an increasing content in SiO_2 extrapolation could be made to the end value 22 $\times 10^{-3}$ cm^3 N/mole and a heat of dissolution of 2,300 cal/g atom.[199]

210. The physical solubility of helium, xenon, and nitrogen in glass melts was again discussed in view of its eminent importance for modern high-vacuum and electronic technology by H. O. Mulfinger, A. Dietzel, and J. M. F. Navarro,[200] chiefly in alkali silicate glass compositions, and over a temperature range from 1200° to 1480°C. The solubility of He and Ne generally increases with a decreasing alkali content. The particular concept is that with increasing temperatures large cavities ("holes") form in the glass melts which are much more important for their volume expansion effects than smaller cavities would be; the cubic expansion coefficient of the holes is a multiple of that of the corresponding melt *per se*. Starting from the structure of high-cristobalite, with its rather loose "open" framework, and silica glass, it is demonstrated that with an infinitesimal addition of alkalies the same functional correlations to the expansion effects are as valid as those observed when the alkali concentrations are high. Models of cluster (swarm) evolution in microdomains of the glass structure were extensively discussed by A. Dietzel, J. O'M. Bockris, H. Franz, and T. Kelen and J. Krogh-Moe *et al.* (cf. Vol. VII. ¶ 311 ff., 323, 482 806) for an explanation of local enrichments in alkalies ions. The strongest increase in hole expansion with increasing temperature is observed in potassium silicate melts, the weakest effect in those of lithium silicates, evidently caused by increasing ionic electrostatic field actions; increasing alkali content is indicated by an increased temperature dependence of gas solubility in glass melts.

211. The importance of such studies on the sorption of rare gases (in the present case only Ar) is most evident by the role which this phenomenon must play in modern gas discharge (Na vapor) lamps, as was demonstrated by A. J. Burggraaf.[201] Such tubes are filled with 98.9 vol. % Ne 1.1% Ar mixture, under a filling pressure of 9 Torr; the measurements are based on the 385–453-m bands for Ar; 585 to 720 mμ for Ne. The mass spectrometry (after 200–500 hours of service) shows a total absorption of Ar in the glass surface. When H_2O vapor is present, the Ar absorption increases rapidly and some corrosion of the surface is observed over a layer thickness of a few 100 Å. Under high pressure[202], up to 10 kbars, and 350° to 950°C, the

[198] Advan. Glass Technol., Proc. Int. Congr. Glass, 6th, Washington, D.C., 1962, Pt. I. pp. 230–248.
[199] On the diffusion constants see Scholze and Mulfinger, *Glastech. Ber.* **35**, (12), 495–500 (1962).
[200] *Glastech. Ber.* **45**, (9), 389–396 (1972).
[201] *J. Amer. Ceram. Soc.* **49** (8), 450–454 (1966).
[202] Cf. S. P. Faille and D. M. Roy, *J. Amer. Ceram. Soc.* **49**, (12), 638–643 (1966).

solubility increases considerably more rapidly than it does at constant pressure and increasing temperatures alone, as is evident from a filling effect in cavities of glass structure (cf. ¶ 210). Rare gases with small atoms (He) but high compressibility, have a higher solubility than have gases with large atoms (N_2). Pure B_2O_3 glass shows the highest solubility data up to 10 mole % for 8 kbar of pressure. When reheated, oversaturated rare-gas solutions in glass melts show immiscibility (i.e., degassing) at lower temperatures for rare-gas solutions, and higher temperatures for chemically bonded water. The nature of the bonding mechanisms involved between the gas phase and the glass is probably essential for the redegassing phenomena, and the minimum temperature required to start; it is evidently highest for the chemically bonded system, in the present case for the systems with H_2O, in a lower degree for CO_2.

212. The difference between physical and chemical solubility is just in the center of the problematics in the valuable publication by H. O. Mulfinger and H. Meyer[203] when these authors studied the solubility of *nitrogen* in glass melts. Seemingly, the true physical solubility of nitrogen is very low, whereas the investigations disclosed that the chemical solubility may be four orders of magnitude higher when the formation of *nitrides* in the course of heterogeneous gas reactions is taken into account. This is made evident by the observation that a 1-hour rinsing reaction of NH_3 in a glass melt at 1350°C is sufficient to evolve in the glass a characteristic infrared absorption band at $\lambda = 3\ \mu$ assigned to a N – H vibration; this fact gives instructive information on heterogeneous gas reactions taking place in the atmosphere existing in a gas-heated glass furnace and demands an examination of reactions in which *nitrides* are temporarily present in the glass melts. Beyond that, investigation is directed to the similar phenomena of the presence of nitrogen and its compounds (perhaps, as nitrides) in magmatic systems containing alkali aluminosilicates like feldspars. The presence of nitrogen in such minerals as ingredients of glass batches was suggested by the ubiquity of nitrogen in the minerals of granites, pegmatites, and syenitic rocks. In a later publication[204] Mulfinger emphasized that the maximum amount of glass dissolved depends on the primary form of nitrogen reacting, whether it is present in the molecules, N_2 atoms, N (as this is the case in the plasma torch flame), or as NH_3 and the like, i.e., chemically bound. A mixture of 80 parts N_2 and 20 parts water reacts at 1400°C with a Na – Ca silicate glass, as an example, to evolve 13.9 cm^3 N_2/cm^3 glass, i.e., dissolved as N_2. When NH_3 reacts with silica in glass melt, the end product will be the nitride, Si_3N_4, formed over different intermediate, H-containing products, as shown in the scheme in Figs. 65–67 for different gas mixtures

[203] *Glastech. Ber.* **36** (12), 481–483 (1963).
[204] *J. Amer. Ceram. Soc.* **49**, (9), 462–469 (1966).

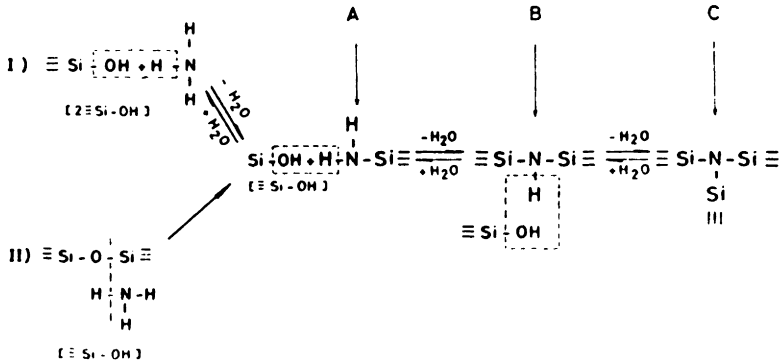


FIG. 65. Reactions of ammonia gas with silicate melts. (Mulfinger.)

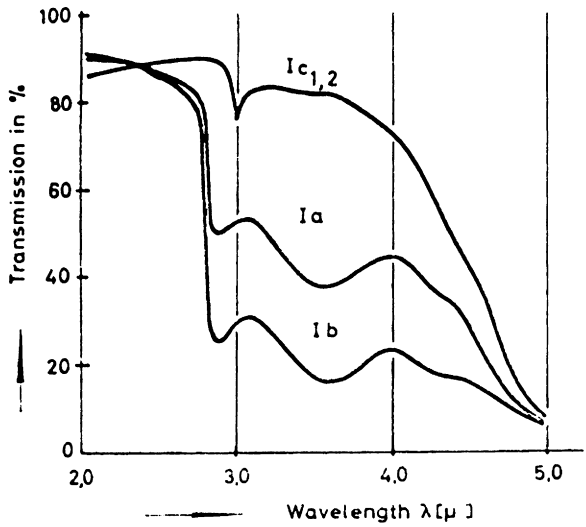


FIG. 66. Infrared absorption spectra of soda-lime silicate glass; (I a) after melting with H_2O for 2.5 hours at 1400°C. (I b) after bubbling with p_{H_2O} of 180 Torrs; (I c) after bubbling with ammonia for 1.5 hours at 1400°C. (Mulfinger.)

bubbling through the silicate melt in different furnace atmospheres (in Fig. 67 also in the presence of some free carbon in the melt batch). Striking differences in the infrared absorption spectra are to be noted here, with variable partial pressures of the gas phases in the furnace atmosphere. On the other hand, atomic nitrogen reacts in the plasma torch flame, is incorporated as dissolved nitride, and causes oxygen to be released. In the presence of CO the amount of chemically bonded and dissolved nitrogen is minute.

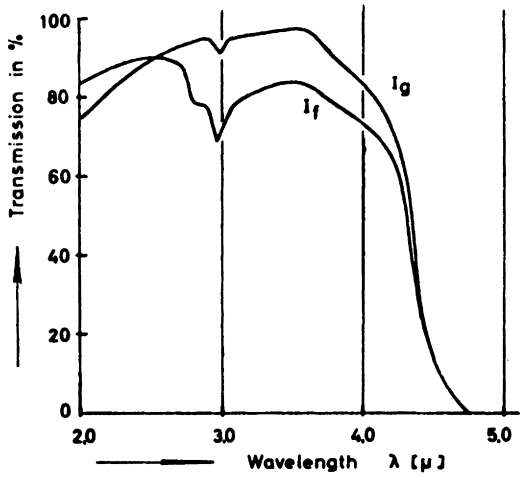


FIG. 67. Infrared absorption spectra of soda-lime silicate glass, after addition of 3 wt.% carbon. (I g) After bubbling with nitrogen for 2 hours at 1400°C; (I f) after bubbling with moist nitrogen for 2 hours at 1400°C. (Mulfinger.)

213. On the basis of experimental observations and conclusions of H. O. Mulfinger as mentioned above, it is not surprising that H. Meyer[205] could detect the presence of chemically bonded nitrogen in the substance of porcelains and their glazes. The repeatedly emphasized primary occurrence of Si nitrides in natural raw materials (especially feldspars and granitic rocks) is in parallel with the synthetic conditions studied by Mulfinger *et al.* The participation of N_2 gas in products of ceramic processes is a well-known fact and exactly explains the "boiling" and "bloating" of feldspar glazes as demonstrated simply and conclusively by H. Meyer[206] by exposing such specimens in the heating microscope (using a shadow-casting "silhouette" method) with industrial raw materials (feldspars, pegmatites, porphyries).

214. On a much broader scientific basis, A. Mitchell[207] compared the infrared vibration spectra of $Na_2O \cdot B_2O_3$ melts with a controlled content of NH_3 or $NaNH_2$, and came to the conclusion that at 1000°C, no $(NH)_n$ bands are stable. Mitchell is inclined to interpret the alleged stretching vibration band of N—H bonds (at 425 mμ) as the principal O—H valence band vibration of adsorbed water. In the case of alkali borate glasses he thought of B—N—B groupings which may appear

[205] *Ber. Deut. Keram. Ges.* **41**, (9), 532–533 (1964).
[206] *Ber. Deut. Keram. Ges.* **42**, (6), 248–250 (1965).
[207] *Glastech. Ber.* **38**, (6), 232–234 (1965).

during the dissolution process. Bridge type B—N—B bonding may be formed with that of the very unstable bonding B—B. When H_2 (formed *in statu nascendi* by thermal decomposition of NH_3) reacts with the borate it opens the way to the insertion of NH groups, e.g., when equally unstable Si—Si bonds are inserted with NH groups into the silicate glass. Tertiary bonding of N atoms with three neighboring B (or Si) atoms (by condensation of NH and OH groups in the borate basis) would end with the evolution of Si_3N_4 or BN.

215. Once again, H. O. Mulfinger and H. Franz[208] bring up the problem of how N can be built into borate or silicate glass melts, especially by analyzing the infrared bands between 2.93 and 3.00 μ which are commonly interpreted as induced N—H valence vibrations. Mulfinger and Franz, however, also discuss a third possibility which was demonstrated by V. M. Kamyshov, O. E. Esin, and S. K. Chuchmarev[209] for $CaO-Al_2O_3-SiO_2$ type slags in reaction with hydrogen and CO_2 bonded with nitrogen in contrast with Mitchell's interpretation. The evolution of N—H bonds (near 3.0 μ) is conclusive, formed after a primary formation of NH_2 which (see above) would react with H_2O to form NH groups + hydroxyl groups in silicate glass, and/or condensation to groups Si—N—Si. Other questions concern how safely one may infer the differentiation of the infrared vibration spectra to discriminate between N—H and NH_2 groups in silicate—nitride systems. Mulfinger *et al.* are confident that the answer is in favor of the theory discussed above, *a fortiori* as seen from observation of deuterated glasses, and those treated with NH_3 to develop NH-containing glasses. In principle, it is important that a conspicuous degree of nitridization of a given glass is only possible by reactions which remove water from an initially given content of H_2O; and conversely for a higher primary water content, only little nitrogen (as NH_2, or NH groups) can be dissolved to form a silicate–nitride composite, whereas at a low-water content (or even an anhydrous system) larger amounts of nitrides are dissolved.

216. The phenomena of nitrogen introduction into different alkali borate glasses proved to be somewhat unexpected. They were extensively investigated by V. A. Ferrandis, J. M. F. Navarro, and J. L. O. Mazo[210] in which, by exposure of the glasses in nitrogen mixed with ammonia gas a series of very remarkable true chemical reactions will occur. We recall again the observations of H. O. Mulfinger and H. Franz[211] in which, depending on the temperature of the glass melts, the formation of boron nitride, BN, is possible and may even become the predominant

[208] *Glastech. Ber.* **38**, (6), 235–242 (1965).
[209] *Vysshie Uchebn. Zaved., Khim. Metallurgiya* **7**, 24–28 (1964).
[210] *Glastech. Ber.* **45**, (9), 397–406 (1972).
[211] *Glastech. Ber.* **38**, (6), 235–242 (1965).

reaction. In the experiments of the Spanish authors, it is remarkable that it made a difference whether the glasses reacted with the ammonia and nitrogen at fusion temperatures, or with glass powders, i.e., at relatively low temperatures. In the latter case, the nitrogen is bonded in three subsequent steps. In lithium borate glasses the formation of BN is nearly quantitative. Ferrandis *et al.*, in general, confirm the observations and conclusions made by Mulfinger and Franz concerning the mechanism of the introduction of nitrogen into the glass substance in different stages, with rising temperature, namely, forming first groups of the $B-NH_2$, then of $B-NH-N$, and last of

$$\begin{array}{c} B-N-B \\ | \\ B \end{array}$$

type, the end state meaning a complete destruction of the borate glass framework structure. Equilibria in the sequence

$$B-O-B + NH_3 \Longleftrightarrow B-OH + HNH-B \Longleftrightarrow B-NH-B + H_2O \overset{+BOH}{\Longleftrightarrow} \begin{array}{c} B \\ B-N-B \end{array} + H_2O$$

are evidently strongly temperature dependent, and determined by the specific nature and concentration of the alkali ions of the borate glasses, reaching at about 1200°C a complete conversion to BN. The evolution of different crystalline phases from the glass matrix in the earlier steps of the sequence is confirmed by extensive X-ray diffraction data and diagrams which demonstrate the increasing formation of BN with rising temperatures.

217. T. H. Elmer and M. E. Nordberg[212] treated *porous* glass at high temperatures with NH_3. Sintered porous glass nitrided in this way *in vacuo* was also prepared. The latter products are characterized by infrared absorption spectra in which the bands of the normal glass appear shifted, the resulting vibration mechanisms being characteristic of N(III) atoms. As a function of the content of N(III) the upper cooling temperatures of the nitrided glasses are shifted (cf. Vol. V.B. ¶ 213, Footnote 459). Another publication of the same authors[213] concerns highly siliceous porous glasses (prepared by leaching reactions as is Vycor glass), or pure silica glass, when these are electrolyzed. The alkali cations migrate in this case to the cathode where they induce local crystallization of cristobalite. But when nitrogen is present in the glass (i.e., after treatment with NH_3) of the same primary type, this crystallization is suppressed, most probably by an intrinsic change of electric resistance in the glass structure containing nitride. Technologically it is interesting to learn from this second publication that the centers observed in the ultraviolet spectral range

[212] Proc. Int. Congr. Glass, 7th Bruxelles, 1965, Pap. No. 30, pp. 1–11.

[213] *J. Amer. Ceram. Soc.* **50**, (6), 275–279 (1967).

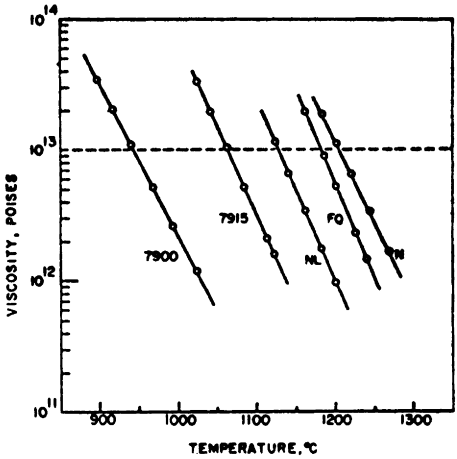


FIG. 68. Viscosity curves for normal and nitrided glasses. Glass No. 7900 contained 96% silica, No. 7915 98% SiO_2 (with less than 0.002% Na_2O); (N) corresponds to nitrided glass, (NL) to nitrided, and then releached glass. The dotted line indicates the viscosity ($\eta = 10^{13}$ P) at the annealing temperature. (Elmer and Nordberg.)

migrate also to the cathode, leaving on the anode side regions of silica-enriched glass of high quality. Concerning the changes in viscosity and the temperature for $\eta = 10^{13}$ P see Fig. 68.

218. *Mass spectrometry* was applied by R. W. Lee and D. L. Fry[214] for investigations of the permeation and (anomalous) diffusion of deuterium (D_2) in Pyrex, Vycor, and OH-poor silica glass, including also a determination of the rate discussion of the exchange reaction $D_2 + Si-OH \rightarrow H-D + Si-O-D$ as a function of time. For the range from 465° to 985°C, the activation energy of diffusion was determined to be 10.4–10.5 kcal/mole, that for the permeation 8.85–9.36 kcal/mole, and that for solubility between −1.1 to +1.6 kcal/mole. From the near-infrared spectroscopic data the ratio of metastable/permanent OH groups could be derived. A model concept for the diffusion of H_2 into silica glass was also established which indicated that the metastable OH groups in the SiO_2 framework resulted from molecular H_2 on its diffusion way into the framework, in agreement with the reaction scheme

$$Si^{4+}2O^{2-} + \frac{1}{2}H_2 = Si^{3+}O^{2-}OH^-$$

It may be that in the environment, surrounding a contamination center may be required for initiating such a reaction. It is also conceivable that large residual Cl^-

[214] *Phys. Chem. Glasses* **7**, (1), 19–28 (1966).

ions which are frequent in silica glass Corning #7940 (produced from $SiCl_4$) are the origin of an anomalous, unusually low permeation and diffusion of D_2 in Vycor glass (prepared from a maternal borosilicate glass), i.e., anomalously increased relative to normal, fused silica glass. Such exceptional phenomena may be referred to smaller B^{3+} ions, in sites of Si^{4+} of normal silica, to facilitate mobility of the hydrogen (or deuterium) molecules.

219. For the diffusion of N_2 in glass, G. H. Frischat and H. Oel[215] applied the same interesting microscopic observation methods which Oel had developed for artificial bubbles migrating in softening glass[216] to determine the shrinking of the bubble diameters at 1100°C maintained for 30 hours, indicating a diffusion coefficient of lower than 6.5×10^{-8} cm²/second, the ratios of the diffusion coefficients for N_2, Ne, and H_2 being approximately 1:50:1000, also in analogy with calculations from the cavity diameter in the glass framework structure.

220. Once again coming back to the problem of the existence of nitrogen compounds in natural silicate minerals (particularly of the feldspar group) and their technological significance, we mention an interesting article by R. Kranz[217] who made explicit gas analyses of the specimens ground to a fine powder in a vacuum at room temperature. Gas chromatography and mass spectrometry gave convincing evidence for the presence of the following gases and vapors:

CH_4; hydrocarbons from C_2H_6 to C_4H_{10}; NH_3
CH_3NH_2; $C_2H_5NH_2$
H_2; Ar; N_2; CO_2; H_2O sporadically probably CH_3F

By a lengthy boiling of aqueous solutions of alkali hydroxides one may extract many of those compounds; the organic amines have been most probably introduced on the way over cation exchange reactions in cooperation of nucleoacids. It is also interesting that Na feldspars contain much less nitrogen than K feldspars, probably from the action of ^{40}K radioactivity, and that of radioactive rare-earth elements which are relatively enriched in cations and organic N compounds.

221. In his most recent investigations, H. O. Mulfinger[218] demonstrated highly promising applications of the *gas-chromatographic* methods for the determination of different gases in gas bubbles in glass, and a thorough derivation of the size frequencies of those bubbles in the volume range from 2.8×10^{-6} to 1×10^{-1} μl. A very ingenious method for sampling the gases from bubbles for the chromatographic analysis cannot be described here in detail, neither can the segregation columns

[215] *Glastech. Ber.* **40**, (8), 311 (1967).
[216] *Glastech. Ber.* **38**, (4), 156–166 (1965).
[217] *Ber. Deut. Keram. Ges.* **44**, (9), 430–435 (1967).
[218] *Glastech. Ber.* **44**, (11), 467–473 (1971).

(working with 5A zeolite filling) and the detector system (preferably based on a very efficient He ionisation detector device). Realizable limits of determination were for H_2: 3×10^{-5} μl; for CO: 8×10^{-5} μl; for CO_2: 2×10^{-6} μl; for O_2: 3×10^{-6} μl; and for N_2: 7×10^{-6} μl. The calibration and permissible inaccuracies of the method are also discussed in detail.

222. The particular value of the methods developed by Mulfinger is made evident in a most recent publication[219] for the gas analyses of bubbles in an alkali Ba silicate glass, sampled at temperatures between 1100° and 1250°C, in their changes as a function of time which make possible conclusions on defined equilibrium conditions for the different reactive gases in the bubbles, therefore, also on the volume shares in different "ages" of the samples during the glass fusion and fining operations. All of the experimental data were taken from real glass plant experience and practice, and are statistically evaluated from a wealth of numerical material. In a comparison of the gas-chromatographic analysis data with those achieved by the mass spectrographic method, the first is superior for distinguishing the behavior of CO and N_2 which have the same molecular weight (28) and therefore their effects are not distinguishable by the second method. On the other hand, the gas-chromatographic analysis is difficult for discrimination of Ar and O_2, which is easy and accurate with mass spectroscopy. Important, in addition, is a consideration of gas adsorption on the inner surface of the instruments, and certain unavoidable dead volume effects (in glass the breaker device for opening the bubbles from the glass samples).

223. The reliability and reproducibility of the gas-chromatographic method applied to the analysis of the gas fillings of fining bubbles is demonstrated very well in Mulfinger's most recent contributions, along with data on the volume shrinkage of bubbles caused by gas reactions and resorption in the glass which give information on the rates of reaction by such volume change effects.

The gas-chromatographic method was also applied by J. Žluticky, H. Štverak, and L. Němec[220], in combination with an improved vacuum hot-extraction device. In distinction from the techniques used by Mulfinger *et al.*, the authors mentioned above chose a heat conductance detector device but a similar two-column separation system furnished with Linde 5A zeolite, and "Synachrome E5", in a carrier gas (purest H_2) flow of 75 ml/minute. For calibration the test gases (CO, CO_2, O_2, N_2, and SO_2) were introduced by a gas injection jet. For the hot-extraction process a temperature corresponding to an optimum viscosity = 2 P of the glass melt and a vacuum of 10^{-4} Torrs is recommended.

[219] *Glastech. Ber.* **45**, (6), 238–243 (1972).
[220] *Glastech. Ber.* **45**, (9), 406–409 (1972).

HYDROGEN IONS (PROTONS), HYDROXYL IONS, AND "WATER CONTENT" IN GLASS

224. One of the most problematic fields of glass technology is the knowledge of the ionic conditions of the so-called "water content", i.e., the role which is played by H^+ ions and by OH^- ions. In this regard, we may, in this respect, refer to previous studies by P. Ehrmann, M. de Billy, and J. Zarzycki[221] who applied the base exchange method for the reactions K^+ or $Na^+ \rightleftharpoons NH_4^+$ between the glass surface and a melt bath of NH_4HSO_4, at 325° to 375°C. For these simple exchange processes, the Fick diffusion law is fulfilled for the amount of exchange ions, M, as a function of the square root of time ($\sqrt{t}$), as long as there are no cracks that start from the surface of the glass and reach into the massive glass. The H^+ ions do not diffuse in the form of protons from the decay of NH_4^+, but as H_3O^+ of the radius 1.40 Å, which, because of its largeness, retard the migration speed considerably. The diffusion coefficients corresponding to a solved H_3D^+ state are $=1.13$ and 0.97×10^{13} for Na– and K–Ca silicate glasses, respectively.[222] In every case, Ehrmann *et al.* came to the conclusion that the NH_4^+ ions, as such, do not participate in the migration kinetics, at least not as long as there is no electric field exerting influence on the base exchange reaction studied by those authors. OH^- ions are then fixed onto the silica skeleton of the framework as long as dealkalinization takes place. The experimental method used by those authors for a direct micrometric determination of the thickness of the typically opaque exchange layer, after the treatment of the glass surface in bisulfate melt, is sufficiently accurate to illustrate the rate in which validity of the Fick law is preserved, i.e., before cracks are evolved and thus to explain the reasons for the anomalously retarded diffusion rates.

225. Ehrmann, de Billy, and Zarzycki[223] made beyond that the interesting observation that a glass surface, when first treated with SO_2 at elevated temperatures to show a dealkalinization reaction, and *then* treated with a melt bath of NH_4HSO_4, at 350°C, shows a different type of change in the surface aspect, namely a "point-for-point" hydrogen ion penetration of the glass, by the appearance of single white points or holes, which continuously are growing into deeper layers of the glass. They have a hemispherical cross section, with a slightly curved concave meniscus. In the measure as H^+ ions are introduced into the massive glass at temperatures below 550°C, the common type of cracks appears, but above 550°C, a tendency to develop star shapes is marked in a layer of about 0.1 μ depth. Infrared absorption spectra

[221] *Verres Refract.* **15**, (2), 63–73 (1961); **15**, (3), 131–139 (1961).

[222] Cf. from the older literature investigations by Ch. B. Hurd, A.A. Vernon, and E. W. Engel, *J. Amer. Chem. Soc.* **49**, 1447–1450, (1927), and N. J. Kreidl, Br. F. Trumm, and R. F. Schott, *J. Amer. Ceram. Soc.* **24**, (7), 225–229 (1941).

[223] *Verres Refract.* **18**, (3), 169–180 (1964).

make it evident that the dealkalinization process is directly correlated to an increasing content of hydroxyl ions which are fixed on the silica-enriched glass framework.

226. One of the central problems to be discussed in this chapter is the *solubility of water vapor* in glass melts of variable basicity. H. Franz and H. Scholze[224] applied *in extenso* the infrared spectroscopic method for the determination of "water" in glasses,[225] Using hydrogen as a carrier gas, Franz and Scholze directed water vapor into glass melts at 1250°, 1320°, 1400°, and 1480°C under a partial pressure of 380 mm Hg, to eliminate changes in the glass composition by alkali volatilization. The results were later recalculated for a pressure =760 mm Hg. For pure silica glass, the vapor treatment was made at 1750°C by surface diffusion through a layer of 1 mm thickness until saturation was reached after about 60 hours. The infrared absorption measurements were made for alkali silicate glasses, embedded, because of their hygroscopy in hexachloro butadiene, and between two plates of NaCl crystal. The free OH bands were those at 2.73 to 2.95, bound bonds were at 3.35 to 3.85; and 4.25 μ. The solubility of H_2O in those glasses increases with rising temperatures and the increasing alkali contents of the glasses. The larger the cation radii, and the smaller the field strengths in the glass constitution, the steeper the increase in water solubility. For constant alkali contents, ternary alkali–alkaline earth silicate glasses show increasing H_2O solubility following for the alkaline earths MgO < CaO < SrO < BaO, but replacement of SiO_2 by Al_2O_3 reduces the solubility every time. The latter is also strongly reduced when Na_2O is replaced by CaO, and when SiO_2 is kept constant. The heat of dissolution is 3000–6000 cals/mole for the binary glasses of system Na_2O–SiO_2, 1000–3000 cals/mole for the ternary compositions.

227. There are striking differences in the results for the solubility of water vapor in the sodium silicate glasses from previous data of C. R. Kurkjian and L. E. Russell[226] who, however, did neither consider nor correct for volatilization of alkali from the glass melts. The ruling mechanism of H_2O dissolution is the reaction $H_2O(\text{gas}) + O^{2-}(\text{melt}) \rightleftharpoons 2\ (OH)^-(\text{melt})$, increasing with activity of O^{2-} ions, i.e., with the *basicity* of the melt. When silica glass was chosen for "neutrality" conditions, the basicity of other glasses can be referred to an equation of the form $\Delta p(O) = 2x\log(x_1/x_2)$, when x is the mole fraction of dissolved H_2O. Typical basicity is shown when the $p(O)$ values have a negative sign, and $\Delta p(O)$ is a linear function of the cation field strength, z/a^2 (Dietzel). $\Delta p(O)$ data derived from the water solubility are, as

[224] *Glastech. Ber.* **36**, (9), 347–356 (1963).

[225] Cf. H. Scholze, Glastech. Ber. **32**, (3), 81–88 (1959); **32**, (4), 142–152 (1959); **32**, (7), 278–281 (1959); **32**, (8), 314–320 (1959); cf. Vol. II.A. ¶ 255–260.

[226] *J. Soc. Glass. Technol.* **42**, 130–144 (1950).

a rule, about one-half of those values calculated from galvanic electric motoric force measurements[227] which had been determined at low (room) temperature. There is, however, a good agreement with basicity data from color titrations[228] compatible with those derived from the solubilities of CO_2 and SO_2.

228. The acidity–basicity conditions, as referred to water solubility in glass melts, were later transferred by H. Franz[229] to B_2O_3 glass melts for which, in principle, the same reaction mechanisms between molecular water (in vapor phase), and O^{2-} anions (see above) are applied, combined with infrared spectroscopic data.[230] In the presence of cations R^{n+}, the O^{2-} ions will then be more intensively bonded to the cations of high field strength (schematically: formation of $R-O^- \ldots$ H), with a proton activity a_{OH} of the hydroxyl ion. Neutrality, i.e., for equality of both activities then corresponds to a minimum H_2O solubility. Strongly hygroscopic oxides like B_2O_3 and P_2O_5 (as glasses) are typical representatives of high acidity, whereas highly basic glasses are, e.g., those of *o*-silicates.[231] The general infrared absorption characteristics of B_2O_3 and SiO_2 are remarkably similar, but the absence of bands near 3.5 and 4.25 μ indicates that the OH groups in B_2O_3 glass do *not* evolve strong bridge bonding; they are bonded only by weak secondary forces of O atoms in the framework structure.

229. Another investigation made by H. Franz[232] concerns the solubility of water vapor in melts of alkali *borate* composition which, in the same manner as shown above, (cf. ¶ 227f) for silicate glasses obey the $\sqrt{t}$ law for the partial pressure which is confirmed anew. With increasing amounts of K_2O and Na_2O, one observes minima dissolved in H_2O contents, namely for glasses of 25 and 35–40 mole % of alkali oxides, but no minimum of the same kind is observed in lithium borate glasses. Nevertheless, in the place of the minimum to be expected in this case, a minimum of water solubility and of the heat of dissolution is observed. All these minima coincide with a "neutral point" which also is valid for equal activities in the acidity–basicity limits (see above). The range of minima also for the halfwidth condition of the infrared OH-absorption spectrum at 2.8 and 2.9 μ is seen from Figs. 69 and 70. We will see in a later text also the volatility effects and the neutrality conditions for

[227] Electrochemical method, by G. Smith and G. E. Rindone, *Glass Ind.* **37**, 437–443 (1956); **37**, 454–456 (1956).

[228] *Glastech. Ber.* **18**, 301–308 (1940); **18**, 353–359 (1940).

[229] *Glastech. Ber.* **38**, (2), 54–59 (1965).

[230] Particularly interesting, is in this investigation, the use of films of 0.12 mm thickness of pure B_2O_3 melt which had to be, because of the extreme hygroscopicity of this substance, at temperatures up to 480°C pressed in a closed device.

[231] Cf. those studied by J. M. Uys and T. B. King, *Trans. AIME* **227**, (2), 492–500 (1963).

[232] *J. Amer. Ceram. Soc.* **49**, (9), 473–477 (1966).

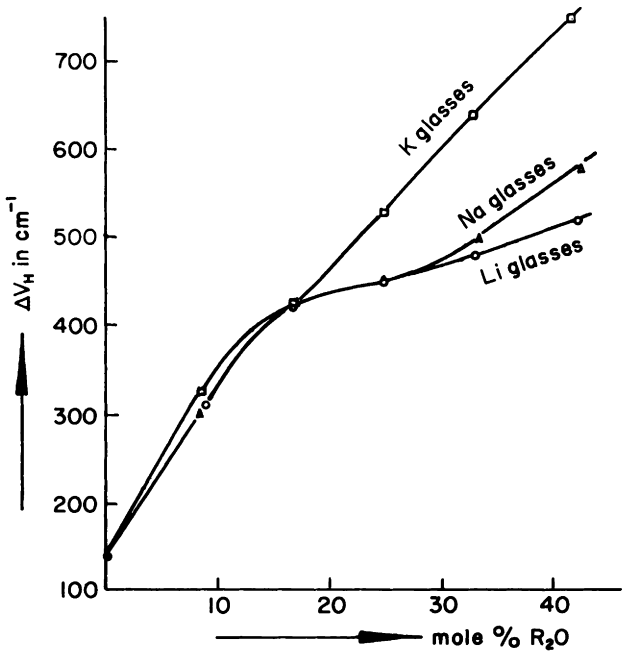


FIG. 69. Half-width of the OH absorption band at 2.8- to 2.9-μ wavelength in the infrared spectra of alkali borate glasses. (Franz.)

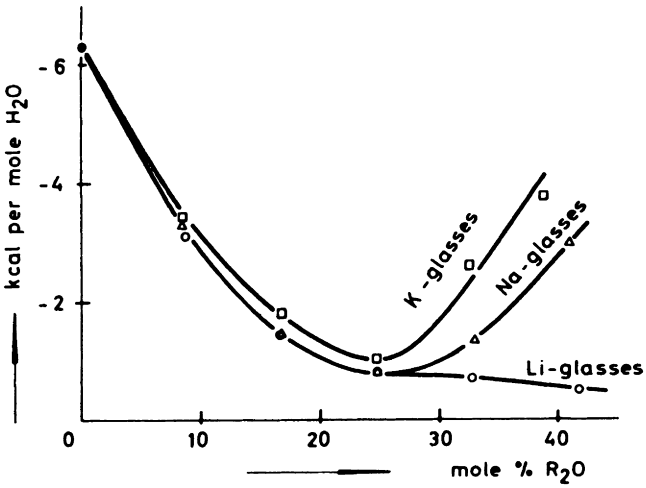


FIG. 70. Heat of solution of water vapor in alkali borate glasses between 750° and 1050°C. (Franz.)

the activities and acidity–basicity properties; there is a rather abrupt transition from the acidic conditions of B_2O_3 on one side—on the basic side for the volatilization of alkalis (cf. Vol. II.B. ¶ 98).

230. Concerning the influence of the water content in silicate glasses on their physical properties, we emphasize here the considerable effects of OH groups in the structure of every given glass on the optical refraction and diffraction parameters and on the density. H. Scholze[233] especially studied the refractive index raising with increasing contents in hydroxyl groups, as determined from the infrared spectroscopy data (Fig. 71). This effect is also observed in the behavior of pure B_2O_3 glass (in contrast with that of SiO_2 glass for which refractive index and density decrease with an increasing number of hydroxyl groups). Scholze presented an interesting interpretation of these phenomena derived from structure particularities of those glasses; when hydroxyl groups are present in simple B_2O_3, B—O bonds must be interrupted. In case of water absorption in such hygroscopic glasses, evidently only a double connection of the B atoms with the surrounding framework will persist, and local structural breakdown near such built-in-OH districts takes place by a compaction of the texture; therefore, increased density and refractive index will be observed. The higher electrostatic charge of central Si^{4+} sites, however, will cause no compac-

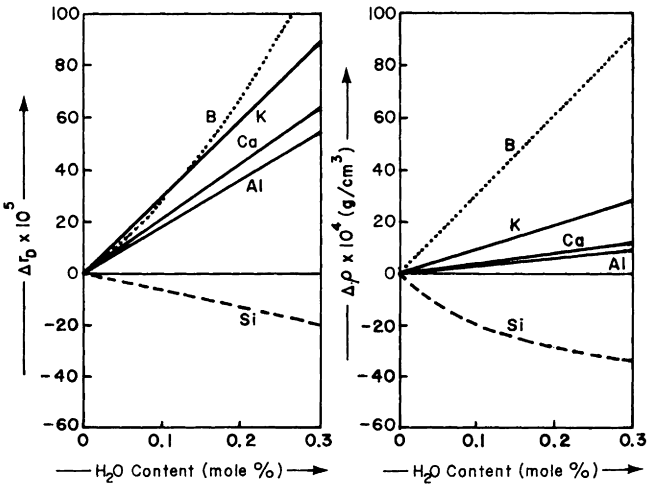


FIG. 71. Change of the refractive index n_D and of density ρ of some glasses with increasing water contents. (Scholze.) (*B*) B_2O_3 glass; (*Si*) silica glass; (*K*) 20 moles % K_2O, 80 mole % SiO_2 glass; (*Ca*) 16 mole % Na_2O; 10 moles % CaO; 74 mole % SiO_2 glass; (*Al*) 20 mole % Li_2O; 5 mole % Al_2O_3; 75 mole % SiO_2 glass.

[233] *Glas-Email-Keramo-Tech.* **19**, (11), 389–390 (1968).

tion in the framework under the action of entering OH^- groups but on the contrary, will cause an expansion and an ensuing decreased density and refractive index.

231. In view of the great importance of infrared spectroscopy for the investigation and application of glass-forming oxide systems and industrial glasses, N. Neuroth[234] published a most useful and handy review of the infrared transmission spectra in a systematic arrangement of diagrams to show the asymmetric valence and asymmetric bonding vibrations, i.e., the effects of atomic displacements and changes in the fundamental valence angles of important glass structures. The diagrams extend to the spectral characteristics of the simplest oxide systems, then to silicates, in comparison with germanate, borate, phosphate, and related compositions, and give a bit of information on nonoxidic glasses. The material presented is supplemented by a brief discussion of the infrared spectroscopic responses induced to the introduction of "water" into glass structures, and of temperature change effects.

232. A highly successful series of investigations was undertaken by J. Götz and Eva Vosáhlová[235] which produced practical recommendations for the introduction of infrared spectroscopic determination of the "water" content of silicate glasses, based on the intensity of the OH bands, over a concentration range from 0 to 0.11 mole H_2O/1 liter glass, by a semimicroanalytical or gravimetric determination of water expelled from glass melts. A comparison of those results shows differences in the extinction data obtained for the OH bands, before and after a drying–rinsing process. The practical use of the molar extinction coefficient, for the band 3600 cm^{-1} is 39.0 liter/mole^{-1} cm^{-1} (cf. previous literature by H. Scholze, 1959, who gave a conventional value of 41.0 liter/mole^{-1} cm^{-1}); for the 2800-cm^{-1} band the same coefficient is 56 liter mole^{-1} cm^{-1}, the Lambert-Beer law is fully applicable.

233. It is very interesting to compare these infrared-spectroscopic results with those discussed by F. Meyer and W. Spalthoff[236] for results obtained by nuclear paramagnetic resonance (npr) methods after which the coefficient was found to decrease with an increasing water content, but constant above the upper limit 0.11 mole/liter as given by Götz and Vosáhlová.

234. More recently, S. C. Kim and L. V. McCarty[237] developed a special computer program for the mathematical solution of rather difficult differential equations for

[234] *Glastech. Ber.* **41**, (6), 243–252 (1968), with more than 120 references from the international literature and instructive numerical tabulated data.

[235] *Glastech. Ber.* **41**, (2), 47–55 (1968); more in details in *Sb. Visoke Skoly chemicko technologicke v Praze* **B.13**, 105–131 (1969).

[236] *Glastech. Ber.* **34**, (3), 184–191 (1961).

[237] *Glass Technol.* **10**, (1), 22–28 (1969).

the general case of a diffusion coefficient which depends on a complex function on the concentration of the diffusion species. This condition is given when "water" will diffuse through the walls, e.g., of the silica glass envelope of incandescent wolfram–iodine filled lamps under about 1 Torr as the upper limit of the inner pressure. Full penetration of the water vapor from the envelope may happen after 9,000 to 27,000 hours of service, when over this period, the wall temperature may be 900°C and the final exterior water vapor pressure may be 30 to 40 Torr. One may think of the possibility that a water "pickup" from the hydrogen–oxygen flame of the torch, which is used to shape the silica glass envelope would bring about exterior pressures that high at a maximum working temperature of 1800°C. In reality, however, this water of foreign origin will contribute only a small portion of the total water which participates in the diffusion process through the glass walls; most of it comes from the moisture of the exterior atmosphere. This would then correspond to the conditions which were valid in the systematic investigations and experiments of G. Roberts and J. P. Roberts,[238] and to the conditions of reaction of the –Si–O–Si bonds with hydroxyl groups, thus to break bonds and to loosen the structure. The conditions ruling in such processes are schematically shown in the diagram Fig. 72. The effects of "fusion" on the inner and outer walls may be seen from Fig. 73 as a function of the theoretically foreseen diffusion time program.

235. We again refer to the important investigations of G. J. Roberts and Z. Haider[239] concerning diffusion studies of "water" into simple similarly silicate and aluminosilicate glasses (among others, commercial plate glass), at temperatures near the transformation range. They have equal importance in comparison to those which

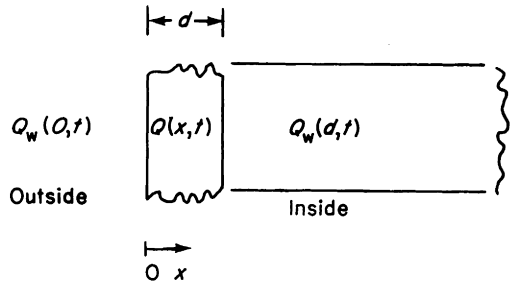


FIG. 72. Schematic diagram of diffusion process of water through the wall of silica glass lamp. (Kim and McCarthy.) $Q_w(0, t)$ = moles H_2O/ml; $Q(x, t)$ = moles OH/ml; $Q_w(d, t)$ = moles H_2O/ml.

[238] *Phys. Chem. Glasses* **5**, (1), 26–32 (1964); cf. Vol. VII. ¶ 478.

[239] *Glass Technol.* **11**, (6), 153–157 (1970); **11**, 158–163 (1970); cf. Vol. VII ¶ 479, 581.

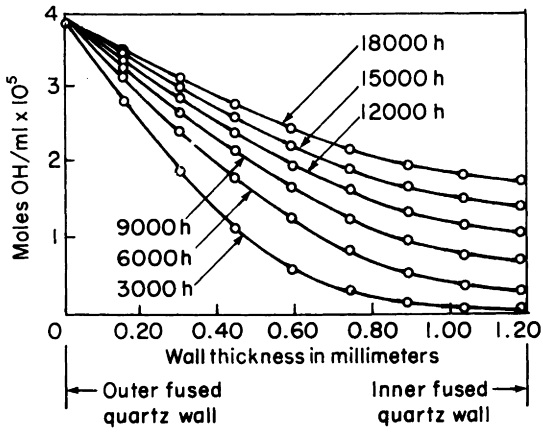


FIG. 73. Hydroxyl distribution in silica glass wall of 500-W tungsten iodine lamp, exposed to 30 Torrs water vapor at 900°C. Assumed average internal temperature is 1280°K. (Kim and McCarthy.)

have been the subject of more complex phenomena, e.g., in silica glass, and practically speaking, in special glass compositions like silica glasses. The mass spectrometric method was used by Haider and Roberts for the study of glass fibers and exterior diffusion of "water"; but also radioactive tracer methods by activation were applied for massive glass samples and inner diffusion conditions. In general, the results in determining the water diffusion coefficients were in good agreement with the theory within the limits of the transformation range, but surprisingly large deviations were found at lower temperatures. Glass fibers, as a rule, showed *higher* diffusion coefficients than those obtained from massive glass. Such conditions may indicate that factors of variation in the rates of cooling, and especially quenching treatments bring about changes in structural effects of thermal-mechanical variables. They also have, therefore, a certain influence on the water diffusion as observed in tritiated water. For binary alkali silicate and ternary aluminosilicate glasses in a temperature range between 450° and 600°C a distinct increase in corrosivity is observed when the ratio $Al_2O_3:Na_2O$ is low. Simple alkali silicate glasses have very similar diffusion coefficients for water, and tendencies to spinoidal unmixing; with increasing ratios $Al_2O_3:Na_2O$ the water diffusion coefficients decrease. The activation energy is reduced to 22 to 15 kcals/mole for an Al-free and another glass with this ratio equal to 1:1, respectively. There are also some similarities to the water diffusion conditions in silica glass when the diffusion coefficients depend on the concentration ratios. Haider and Roberts finally discuss a series of possible diffusion mechanisms for an interpretation of their observations.

236. Among other possible practical problems related to the "water" content and

diffusion behavior of Na – Ca silicate glasses, J. Götz[240] speaks of the heat of water dissolution (= 2.86 kcal/mole) in the range from 1200° to 1500°C for which the dissolved water content is proportional to the square root of the water vapor partial pressure. The water content (or partial pressure) in the combustion gas atmosphere of the glass fusion furnace (cf. ¶ 31) rules the water content of the glass product which, therefore, cannot be controlled by the water (moisture) content of the batch mixtures that only play a rather subordinate role (cf. ¶ 6). The water diffusion from the furnace atmosphere into the glass is in every case a relatively rapid process (cf. Vol. VII. ¶ 483). We also concur with the suggestion of J. P. Poole[241] that in connection with the problems of glass workability, the ubiquitous role played by the water content of industrial glass is not considered far enough, it has not been investigated anywhere near sufficiently, and much intensified future work is necessary.

[240] *Glastech. Ber.* **45** (1), 14–18 (1972).
[241] *Glass Ind.* **48**, (3), 129 (1967); **48**, (3), 132–136 (1967).

Chapter IV

Part A: Technologically Important Physical and Chemical Properties of Glasses

VISCOSITY, RHEOLOGY, PHENOMENA, AND EFFECTS

237. On the wide field of applications of different working processes, not only for the production of industrial glass, but also for its shaping, we may again refer first to the classical book by W. D. Kingery[1] in which P. Loewenstein[2] contributed a special chapter on possibilities for learning methods from practical metal working that can also be applied in ceramic and glass manufacturing. We also refer to Vol. VII. ¶ 26 for the more specialized recommendations of I. I. Braginskiĭ,[3] on the general theory of glass shaping which emphasizes the physical theory of moderately and highly viscous rheological systems to which the industrial glasses certainly belong, with highly developed automatic forming and molding machines. When the viscosity in its variation with time can be regarded as constant over permissible intervals and when the maximum viscosity before the beginning of the forming process is also known, one may easily define a maximum deformation time as a characteristic parameter. On the other hand, one may start in the theoretical treatment of the impending problem from the required total deformation, and define, in addition, a deformation time as a function of viscosity and stresses, thus developing for that a differential equation. The intersection points of the representative curves of both parameters, as graphically determined, mean an optimum viscosity change with time as a measure of the cooling rate, and the commonly used qualitative measure of what is conventionally called the glass "length."

238. For the experimental techniques of viscosity measurements, we may again emphasize the development of *standard glasses* as an indispensable requisite for the

[1] "Ceramic Fabrication Processes", 235pps, Wiley, New York, 1958.

[2] "Ceramic Fabrication Process," pp. 195–198, Wiley, New York, 1958.

[3] *Steklo Keram.* **24**, (5/6), 241–245 (1967); (in Eng. transl.).

calibration of viscosimeters. These glasses are offered by the National Bureau of Standards, specially prepared for this purpose in commerically available samples.[4]

In view of the continuously increasing flood of publications on the viscosity of industrial glasses, we are, of course able to discuss here only a rather arbitrarily chosen number of experimental investigations. We may begin with lead silicate glasses and their analogs of borate, phosphate, and related types, which are particularly attractive for our purpose.

239. First, we may discuss a series of experimental measurements on the important system $K_2O - PbO - SiO_2$ and their melts as published by M. G. Frohberg and W. Rohde[5] which concern the ternary range from 0 to 60 mole % PbO; 0 to 40 mole % K_2O; and 40 to 80 mole % SiO_2, over a temperature range from 800° to 1200°C, which is also of metallurgical interest (cf. Vol. II.C. ¶ 51 ff.). Although K^+ and Pb^{2+} cations are similar in their atomic radii, they are very different in their electrostatic and polarizability characteristics. The results of measurements by a common rotation viscosimeter cover a variation range for viscosity from 3 to 5 $\times$ 10^4 P, and for a constant ratio Si:O, i.e., the number of nonbridging O atoms. The viscosity of the alkali-rich melts even at 1200°C is by two orders of magnitude higher than that of Pb-rich silicate compositions. Such phenomena cannot be convincingly enough interpreted by a common theory of bond disruption effects in the glass structure. For this reason, Frohberg and Rohde also did not attempt to explain the unusually strong temperature dependence of the activation energy of viscous flow. Nevertheless, the *screening* theory (as presented by E. Plumat) gives a certain illustration of functional relations between viscosity and fusion behavior of the K – Pb silicate glasses, having in view, the much different polarizabilities of K^+ and Pb^{2+}, and their effects in the formation of anionic silicate complexes, probably of annular configurations.

240. For an improvement of a convenient use of diagrams showing the logarithmic graphic evaluation of viscosity–temperature data in the direction of possibly linear representations of those important correlations, the method of da Andrade (cf. Vol. VII. ¶ 140, footnote 279) is not satisfactory. Recently, A Andrieu[6]) rediscussed this important problem by calculation of an equation with only two constants, i.e., two experimental points are sufficient for the characterization of a given glass species for the range of log η from 2–5. Andrieu derived a second equation

[4] Cf. Nat. Bur. Stand., prepared stand. glass No. 710, a type Na – Ca silicate glass; basic measurements of high accuracy were made by A. Napolitano and E. G. Hawkins, cf. *J. Res. Natl. Bur. Stand Sect. A* **68**, (5), 439–448 (1964); cf. VII. ¶ 139.

[5] *Glastech. Ber.* **37**, (10), 453–459 (1964).

[6] Compt. rend. Congr. Int. du Verre, Bruxelles, 1965, II.2/69, pp. 1–12.

based on double-logarithmic correlations of viscosity with temperature, for which the graph is linear, and makes possible a rapid orientation of the "length" of the given glass. M. B. Volf[7] applied the method of Andrieu very successfully to a series of borosilicate glasses, working a good agreement between calculated and experimentally determined viscosity data. The second equation of Andrieu gives even better information concerning the workability of a given glass over an arbitrarily chosen temperature range, than the function after da Andrade.

241. The high viscosity ranges ($\eta = 10^{12}$ to 10^{14} P) were studied by J. E. Rapp and C. L. Babcock[8] who developed a modified fiber elongation apparatus, and a calculation method approximating the equilibrium viscosity versus temperature curve in the range from 420° to 800°C.[9] In this way, it is possible to find quickly orientation on the viscosity characteristics of a given glass, from a single fiber measurement, accurate enough to control industrial annealing and thermal treatment processes. Most important is a calibration on the basis of the standard equilibrium η/T curve when problems arise in glass production which require stabilization and standardization in plant operation. The method is doubtless more convenient than that developed by F. H. Norton.[10]

242. According to V. Gottardi, B. Locardi, A. Blanchini, and P. L. Martini[11] (cf. Vol. VII. ¶ 803) lead silicate glasses of the system $K_2O-PbO-SiO_2$ contain particular compactions of the structures when in these compositions, the ratio Si:O corresponds to a maximum microhardness, and a minimum of volatilization at higher temperatures, combined with minimum in the reductibility of PbO. The temperatures of these condensation phenomena are individual functions of the compositions and are much different. When K_2O in such glasses is replaced by Na_2O, the Si:O ratios required for the occurrence of this apparent structural anomaly have higher values than those for corresponding K_2O-PbO silicate glasses, and reach a maximum of compaction. In this difference between K^+ and Na^+ ions bonded into the glass structures, the influence of the higher polarization effects exerted by Na^+ over K^+ find their explanation. When the temperatures are further raised beyond a certain limit, the compaction effect again disappears.

243. M. Bourbon[12] described a device for the simultaneous measurements of viscosity and electric conductance of glasses. The viscosimeter is of the commonly used two-cylinder coaxial arrangement type (the inner cylinder in this case is driven

[7] *Sklář Keram.* **17**, (3), 66–69 (1967).
[8] *Bull. Amer. Ceram. Soc.* **46**, (8), 741–744 (1967).
[9] Cf. the classical J. T. Littleton and R. H. Roberts correlation $\eta d^2(dl/dt)$ = const.
[10] *Glass Ind.* **16**, (5), 143 f. (1935), and the ASTM Stand. Strain Test C 336–64 T(1936).
[11] *Glass Technol.* **9**, (5), 139–144 (1968).
[12] *Verres Refract.* **22**, (4), 385–391 (1968).

electrodynamically by a four-pole asynchronic motor with $\pi/2$ phase displacement), the rotations being digitally recorded by a photoelectric cell measuring between 10^1 to 10^4 P, the electric resistance over a range from 0.2 to 10^4 Ω, with an automatic control of impedance, and a voltage control for the action of the motor between 10 and 100 V.

244. A highly fascinating new construction of a viscosimeter for industrial testing of special glasses for vacuum electronic tubes and the like was extensively described by P. Romann[13] especially for the testing of pasty glasses in the range from 10^5 to 10^{13} P which, for the common viscosimetry, creates tremendous experimental difficulties namely in the neighborhood of the Littleton softening point ($\eta = 10^{7.65}$ P). The moving parts of Romann's instrument consists of a horizontal axis inside a cylinder which is open on both ends, the glass sample filling the space between axis and cylinder surfaces. The cylinders are made of metal alloy Inconel. This arrangement fully guarantees strictly cylindric symmetry of the whole unit making dispensable the Margules corrections in the calculation of viscosity in the rotation-type instruments. Very ingenious is the mechanism construction for the heating and correct placement of the glass sample between axis and the open cylinders, namely, by introduction of two graphite pistons from both sides in vertical position of the axis to make a very tight and reliable fitting of glass and Inconel container system. The viscosimeter, after the introduction of the recipient, like a cartridge fixed in a gun, works after the Couette principle, i.e., by an axial torsional rotation which can be accurately measured by the (here not to be described in constructive detail) system of indicator of the torsional angle over a scale which is calibrated in exponential numerical units. The entire instrument works highly precisely because of a very homogeneous distribution of the temperatures over the length of axial dimensions. To avoid any adhesion of the glass in its pasty state and the metal construction parts, the whole system works in pure nitrogen. The necessary wide range of torque angles to be used in the practice of the viscosimeter after Romann, is reached by a precision-driven motor-device which makes it possible to vary the one-rotation time from 1 to 625 seconds. For the quite specialized purposes to which the instrument is to serve, the dimensions of all the parts have been adapted to those conventionally used, e.g., for the glass for high-frequency electronic tubes.

245. Another really typical plant-adapted viscosimeter for current composition control of the glass, simplified to endure even relatively violent manipulation conditions is that developed by T. T. Carr[14] working after the principle of glass fiber elongation, at a conventional temperature, e.g., of 623.5°C and for viscosities between

[13] *Verres Refract.* **22**, (4), 392–398 (1968); cf. Vol. VII ¶ 135.
[14] *Glass Ind.* **50**, (5), 240, 242–245 (1969).

10^{10} to 10^{18} P, and softening points ($\eta = 10^{7.65}$ P), also nearly only for "one-point" measurements, i.e., for a rapid control in plant survey.

246. An excellent monograph of high value for the engineer's daily use, published under the auspices of the International Glass Congress Subcommittee A.IV,[15] includes a complete literature bibliography up to 1968, with Section I: for Viscosity in the Glass Manufacturing Process; Section II: Viscosity Reference Points; Section III: Bibliography. For every part of this really indispensable monograph the direct emphasis of the presented material is given in practice (cf. Vol. VII. ¶ 37).

ADHESION OF GLASS ON HOT METAL SURFACES

247. As we mentioned only briefly in the description of the Romann viscosimeter (¶ 244) the contact behavior of pasty glass in working machines can develop difficult practical problems because of an undesirable tendency of the glass surface to stick on a metallic surface. This must be considered, in blowing processing with modern bottle glass producing machines. For an examination of such sticking processes, H. Oel and Astrid Gottschalk[16] used a very simple device (Fig. 74) in which the adhesion temperature of glasses on a steel plate was measured under a load of 1 kg/cm^2, and the separation from the glass surface under the drawing force of 150 g/cm^2, the critical "sticking temperature" being the limit of adhesion between the two phases. The device worked for window glass in contact with a fine-ground surface or even highly polished, cast iron, nickel, and platinum: Pt–Au alloys, with the highest adhesion temperatures and nickel-plated, flame-sprayed cast iron, not much different from common cast iron. A commercial chemical instrument glass (Ba borosilicate) shows considerably higher temperatures on cast-iron and much higher on massive nickel. Oil–graphite lubrication and application of a nitrogen–hydrogen atmosphere raise the adhesion temperature by building up a vapor interlayer and a protection skin of graphite. The nobler the substrate metal, the higher the adhesion temperature and the lower the wetting effect.

248. The sticking temperature was tested in a similar way by A. Smrček,[17] not only for a great number of metals and alloys (with different surface rugosities or covered with oxidation products), but also for different lubricants (cf. Vol. VII. ¶ 187, 883). The effects of sticking were particularly striking when the metal surfaces were strongly corroded and evolved reaction gases. The glass composition has a relatively

[15] Inst. Natl. du Verre, Charleroi (A. Cole, ed.), 146 pp., Inst. du Verre, Paris, 1970.
[16] *Glastech. Ber.* **39**, (7), 319–323 (1966).
[17] *Silikaty* **11**, (3), 267–277 (1967); **11**, (4), 339–344 (1967); **11**, (4), 345–351 (1967).

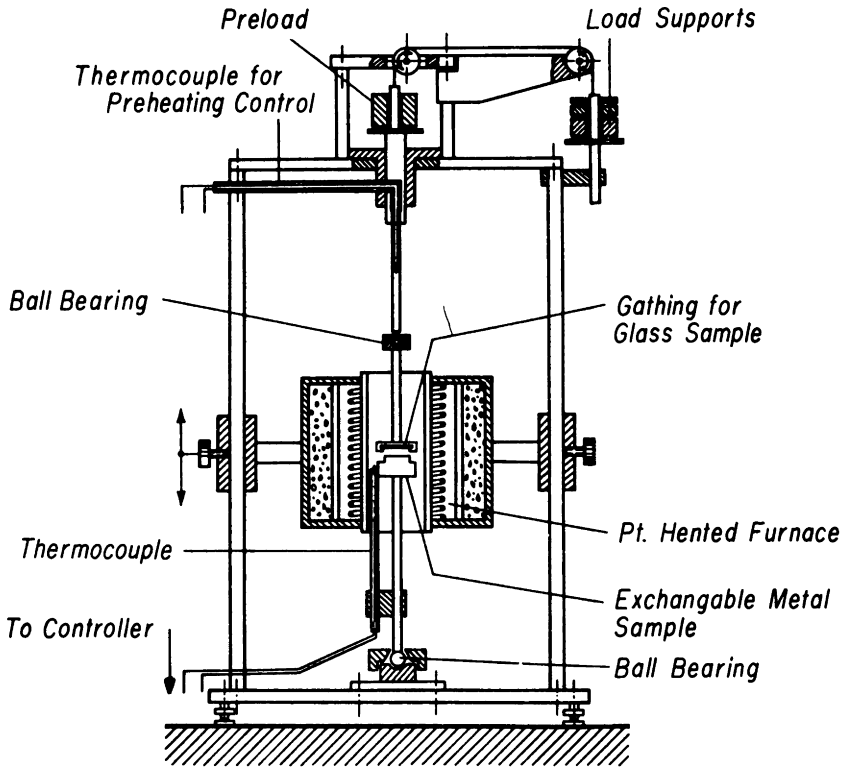


FIG. 74. Apparatus for measurements of the temperature of glass sticking on hot metal surface. (Oel and Gottschalk.)

subordinate effect on the intensity of sticking and on the surface tension. For the sticking temperature of variable glasses with lower viscosity, a tendency is observed to show adhesion earlier than others with a higher viscosity. The adhesion temperature, as such, corresponds approximately to the empirically determined sintering temperature, and the temperature of thermal deformation in the glass surface. Other measurements made by Smrček concern the intensities of pressures applied onto the glass surface, and the length of time this load was exerted. An empirical equation is calculated for the type $\log \eta = 0.81 \log p + 1.10 \log t + 6.08$ (p the pressure, t the time period of contact maintained). Smrček estimates that the influence of chemical bonds to be formed between the metal and glass phases is relatively subordinate, but that van der Waals forces must prevail in the sticking mechanism to develop a certain "pasty flow" over micro-unevenness of the surface.

249. The J. Séjournet (1956) process of shaping by extrusion from a steel

nozzle is another important paradigma in which the glass melt is used as a lubricant for the steady flow of the plastic metal, at corresponding high temperatures. L. Žagar and G. Schneider[18] characterize the technological process as the type in which the glass (e.g., window glass or molten borax) may be packed into the extrusion-shaping mold in the form of loose glass wool, in woven laminates, or "sockets" or "mandrels," or in powder cartridges. The best effects of such a lubrication may be observed for a viscosity in the range from 10^2 to 10^3 P, as found from a heavy lead Flint or lead borate glass, also for phosphate glasses which, at the same time, improve the wettability of the metal surface. Such glasses must have a good solubility for iron oxides to dissolve unavoidable iron scale formed on the hot metal surface on cooling. Such reaction glasses promptly spall from the metal. We also have to supplement some remarks on the more recent successful attempts in industry[19] to replace the silicate melts or related inorganic glasses by high-temperature stable silicone oils (phenyl siloxanes dissolved with toluene or in mixture with Si–graphite, for improving the slipping of the contact between both phases.

250. The importance in glass technology of such gliding or slipping phenomena as rheological reactions on the glass/metal contact surfaces was mechanically analyzed by W. Trier and F. Hassoun[20] as a function of the important angle of inclination of the gob glass shape gliding over a metal surface, the temperatures of the different phases, and the material rugosity. Also, in this case, the validity of specific optimum effects of the lubricant and its nature are of great technological significance, e.g., for the outflow of glass from metal channels. Occasionally, in this case, some lubricant will *not* decrease the friction. A principle sketch (cf. Figs. 75 and 76) may demonstrate a different behavior of gliding flow conditions for a non-

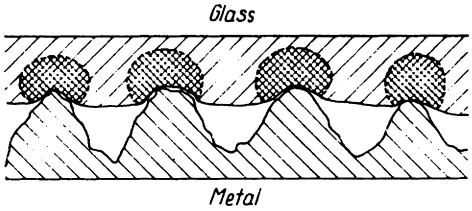


FIG. 75. Schematic representation of contact development between an uneven, and nonlubricated cold gutter and glass. (Trier and Hassoun.)

[18] *Glastech. Ber.* **41**, (11), 446–450 (1968).

[19] Cf. F. B. Kuzyakina, *Steklo Keram.* **25**, (7/8) 409–412 (1968) (Eng. transl.); see also Gh. Gavriliu, *Ind. Usoara* **16**, (6), 381–387 (1969).

[20] *Glastech. Ber.* **45**, (6), 271–176 (1972).

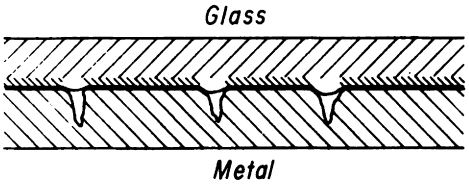


FIG. 76. Schematic representation of contact development between an even, but nonlubricated and cold gutter and glass. (Trier and Hassoun.)

lubricated channel of high rugosity on the surface; Fig. 76 shows another channel with a very smooth surface, also not lubricated, the only contacts existing on some peak elevations, with the cooling effects starting from these as indicated in Fig. 75 by the cross-hatched marking, at relatively low temperatures.

251. Another highly valuable theoretical analysis of the thermal and geometrical conditions of contact for glass/metal which is fundamentally important for the technology of glass shaping was presented by P. Costa[21] in a calculation of the heat flow density on the contacts. The heat transfer from the hot glass into the mold, in respect also to the influences of the profile, is evident. An optimum heat contact is foreseen by theory when grooving in the metal surface to a depth of about 20 μ has been applied, i.e., when the surface of the pressing tool is modeled to a pattern of sawblade-like groove systems, indented into the metal. In the light of Costa's deliberations, it is interesting that the common assumption of coherent so-called "gas pillows" on the contacts and the surface of mold surfaces in glass-blowing forms here cannot be valid.[22]

WETTABILITY AND CORROSIVITY OF GLASS MELTS IN CONTACT WITH METALS AND CERAMIC REFRACTORIES

252. For many special purposes of metal–ceramic and electronic-industrial manufacturing the wetting phenomena of chromium, titanium, zirconium, and "stainless steels" (e.g., the steel 1Cr – 18Ni – 9Ti) have a nearly everyday meaning when these metals and alloys come into contact with silicate metals.

From the abundant literature in this field, we pick out a few illustrative publications: K. Visotskis[23] describes protective coatings of metals with a composite of refractory metal powders as the filler material and a silicate glass as the binder. By

[21] *Glastech. Ber.* **45**, (6), 277–287 (1972).

[22] *Glastech. Ber.* **32K**, 1117–1125 (1959); E. Deeg, *ibid.* **32**, (10), 402–413 (1959).

[23] *Zh. prikl. Khim.* **39**, (7), 1531–1533 (1967) (Eng. transl.).

experimental trial and error it was possible to find from case to case combinations with an optimum efficiencey. In the same problem field is the wetting of refractory ceramics by molten glass and slags (cf. Vol. II.C. ¶ 57, 85, 92), as illustrated from plant experience by S. Minowa, M. Yamada, M. Kato, and K. Nishizaki,[24] by direct measurements of the surface tension of molten phosphate glasses and synthetic slags of the system $CaO-Al_2O_3-SiO_2$, using the sessile drop method on plates of graphite, or refractory oxides, in the classical way (cf. Vol. II.A. ¶ 94 ff., 103 ff.).

253. A very particular glass-technological problem is the strong corrosion effect exerted by volatilized alkalies (preferably of Na_2O) from the refractory walls of the glass tank furnace which was extensively studied by A. V. Morsanyi[25] (cf. ¶ 190 ff.) especially for silica bricks mounted in the superstructure of the glass furnace, in neutral, oxidizing, or reducing gas atmospheres, at 1350°C. The most intensively corrosive character is shown by sodium sulfide (under reducing conditions in the surrounding), and then by sodium carbonate and sulfate (in oxidizing environment). In the latter case, the presence of water vapor accelerates the corrosion reactions. The reactivity of alkali chlorides, also of sodium phosphate is only slight. A moderate increase in corrosion effects is observed when the temperature is raised from 1350° to 1450°C, but sulfur dioxide does not markedly attack. The practical consequences of these observations are visible chiefly in the roofs (the superstructure) of glass tanks at temperatures from 1400° to 1600°C, with an intense slagging of the innermost bricks of about 10 mm in thickness in which at 1450°C the amount of molten material may reach 50%. Since the alkali-rich melt phase currently is running off the roof, the alkali concentration, as such, cannot be used as a reliable measure for the wear deterioration of silica refractory materials (cf. Vol. V. B. ¶ 203 ff.).

254. F. Pernot and C. Kojima[26] (cf. ¶ 654) emphasize the excellent impermeability of gases and liquids of commercial products called "amorphous carbon" in a "glassy" state (in distinction from commercial graphite which has a much higher permeability[27] with a maximum application temperature of 3000°C, and a much higher chemical durability, even in an oxygen-containing furnace atmosphere. Lead glass melts are repelled when brought into contact with "amorphous carbon." Pernot and Kojima present abundant data material on durability tests of all kinds, specifically with molten alkali hydroxides and industrial glass melts. It is mostly undesirable when blackish stained spots appear on the glass, or finest lead metal drop-

[24] *Nagoya Kogyu Gijutsu Shikensho Hokoku* **17**, (6), 127–132 (1968).
[25] *Glass Technol.* **7**, (6), 196–202 (1966).
[26] *Verres Refract.* **20**, (5), 343–353 (1966).
[27] Cf. J. Paresot, *Rev. Haut. Temp. Refract.* **1**, (2), 3–18 (1964).

lets are included, or even when corrosion channels are eaten through to the glass surface, as may occur in potassium–lead silicate glasses which, however, may be mitigated by an aftertreatment remelting in an oxidizing atmosphere, or with molten sodium nitrate. For the fusion of optical glass, therefore, the "amorphous carbon" cannot be a promising material for crucibles or other containers. Pernot[28] extended his studies on the optimum conditions for the production of glasses containing heavy elements, e.g., two silica-free compositions:

(1)	59 wt. % Sb_2O_3	(2)	90 wt. % Sb_2O_3
	12 wt. % PbO		10 wt. % Ti_2O_3
	29 wt. % PbF_2		

in many refractory oxides as crucible materials of commercial availability, with emphasis given to the use of such melting practice for the production of special glasses of increased infrared transmissivity to about 7.9 μ (for sintered) and 7.2 μ (for recrystallized alumina) as the empirically best-suitable commonly available.

255. The corrosiveness of "Corhart ZAC" tank blocks by melts of common Na–Ca–Mg silicate glass was studied by T. Lakatos and J. Simmingsköld[29] under equal viewpoints at 1400°C, using rotating rods of the reference material. The corrosion by the Na–Ca–Mg silicate glass is a linear function of the molecular concentration in the alkali–alkaline earth oxides; alumina does not modify the corrosion mechanism when it is present in concentrations below 10%; corrosion and viscosity increase when the content in MgO is systematically substituted by CaO. The same authors[30] examined the corrosion durability of refractory pot clays to molten glasses (fifteen different compositions). The corrosion brought about by Na_2O is two to three times more than that by K_2O. The corrosion by CaO is a cubic function of its concentration. Siliceous clays bring about 1.5 times more corrosion than aluminous clays do. Lead oxide has no significant corrosion effect, acting more like a kind of diluent; indirectly, it even reduces corrosion. Lakatos and Simmingsköld are of the opinion that the glass viscosity rather than specific chemical reactivity is the most important factor determining the intensity of corrosion. The porosity of the refractory samples of alumina–silica is also an influence. Among the clays chosen for the experiments, it must be considered that the basic clay had a porosity of only 2%, whereas the acid clay had one of 18%.

256. Another constant problem in glass manufacturing is the corrosiveness of a potassium–lead silicate glass (with 5–50 wt. % PbO) on commercial refractories.

[28] *Rev. Haut. Temp. Refract.* **1**, (3), 189–196 (1964).
[29] *Glastek. Tidskr.* **22**, (5), 107–113; (1965); *Glass Technol.* **8**, (2), 43–47 (1967).
[30] See Glass Technol. **8**, 1967 (2) 43–47.

An example of such new tests, in comparison with analogous corrosion phenomena with Na – Pb silicate glasses onto alumina–silica refractories, fusion-cast alumina blocks, and alumina–zirconia (ZAC) was described by G. Bonetti, T. Toninato, A. Bianchini, and P. L. Martini,[31] using the elementary dipping method. As a reaction product (corundum and ZrO_2 = baddeleyite) in the special case of the dense zircon brick material, the formation of wadeite, $K_2ZrSi_3O_9$, (cf. Vol. V.B. ¶ 165, 169) is remarkable. J. Löffler[32] examined the corrosion products of Corhart (fusion-cast) blocks in reaction with Fourcault plate glass melts, among which corundum, nepheline, carnegieite, and manyfold glassy border contact crystallized phases are important (cf. ¶ 183 ff.)—among others, e.g., a "eutectic" mixture of quinary composition (system $Na_2O - CaO - MgO - Al_2O_3 - SiO_2$). A migration of Na_2O from the melt into the surface of Corhart blocks is characteristic. A particular problem is that liquids seeping out from the Corhart blocks at high temperatures easily contaminate the glass and cause striae and other heterogeneities; mullite is relatively scarce in such reaction glasses, however.

257. Special studies on the behavior of industrial magnesite bricks and their changes in physical properties (like thermal expansion and their behavior in the long-period fatigue test) were made by H. E. Schwiete and Fr. Schinnerling,[33] particularly in respect with the chemical composition of commercial magnesites (in two groups, the first with 89 to 92% MgO, the second with above 98% for special materials). The bricks of the second class have a higher refractoriness under load, whereas, the density, porosity, gas permeability, and the modulus of rupture at room temperature are only little influenced by the chemical and mineralogical composition.

258. On a wider field of 20 different glass compositions, including normal Na – Ca silicate and borosilicate glasses, further glass for the fiber production and special modern glasses for the television and electron tube manufacturing industry, J. Recasens, A. Sevin, and A. Gardiol[34] (cf. ¶ 191) referred to the corrosive reactivity of their melts with refractory brick materials, like Corhart, ZAC, and densely sintered zircon tested in a rotary kiln,[35] given different dynamic and static tests over variable time periods of exposure. Again, the development of "stones" (cf. ¶ 74, 191) is frequent in this interesting experimental series; densely sintered zircon proved to be superior to all the others, being corrosion resistant in contact with alkali-free

[31] *Proc. Brit. Ceram. Soc.* pp. 29–40, Aug. 1969.

[32] *Glastech. Ber.* **42**, (9), 363–368 (1969).

[33] *Arch. Eisenhuettenw.* **40**, (11), 881–883 (1969); see also a report on a Symposium by the British Glass Industry Research Association, Sheffield; T. S. Busby, *Glass Technol.* **7**, (6), 181–186 (1966).

[34] *Verres Refract.* **23**, (1), 19–27 (1969).

[35] Cf. P. Bortaud, *Silicates Ind.* **22**, (10), 443–446 (1958).

borosilicate glass (cf. Vol. II.C ¶ 19 ff.). From practical viewpoints, an empirical classification of high-quality refractories for glass furnace operation was proposed by Recasens *et al.*, which comprises different classes of qualities but abandons the classical principle of a systematics after the chemical composition of the refractories.

259. The electron-beam microprobe techniques proved to be an excellent and reliable tool for studying and solving industrial problems of corrosion by glass melts in refractories for tank walls, as K. Konopicky, H. Lindley, Fr. Gebhardt, and M. Baum[36] demonstrated by special investigations on the uppermost layers of regenerative systems (piles). The refractory material in these piles is exposed to strong corrosive reactivity of batch dust from the fusion chamber of the glass furnace, and to the action of volatiles like V_2O_5 from fuel oil ashes (cf. Vol. II.C. ¶ 84). Konopicky studied extensively the inclusions of Cr_2O_3 derived from tiny crystals of the tracer mineral chromite in many glass sands, which are a most troublesome anomaly of glass production because of the persistency of these oxidic contaminations of a high staining power. The microprobe, in combination with the electron microscope, is also an important help for the distinction of such oxides like chromite which may occur in residues from resorbed magnesite refractories in the regenerative pile. The common mineralogical examination of these and related inclusions may easily detect the occurrence, e.g., of green-stained olivines or yellow-stained diopsides, indicating the source of many anomalies.

HEAT TRANSFER BY CONDUCTANCE AND RADIATION IN GLASS FURNACE OPERATIONS

260. The measurement of the local heat transition in turbulent friction-layer systems, as a function of compulsive convection conditions was studied by E. Achenbach.[37] These are of greatest practical technological importance for the multiple heating-up and cooling processes in the course of manufacturing. A particularly useful instrument for measurements in this discipline proved to be the application of fluid-dynamic pressure-heads like the Preston tube (tangential stress probe) with a turbulent flow over a wall surface. The aperture of the tube must be directed against the plane of flow. The manometric measurement of the dynamic pressure against the flat-lying plane of the tube takes place together with that of the density of the heat current, e.g., in the surface of an air-cooled glass machine die. The integration of differential equations valid for this density of the heat currents and a temperature gradient delivers "universal" curves for the calibration of the

[36] *Glastech. Ber.* **42**, (9), 368–374 (1969).
[37] *Glastech. Ber.* **39**, (4), 217–225 (1966).

Preston tube, and therefore, also of the local heat transfer coeffiient associated with profiles of pressure gradients, large temperature differences, surface rugosity, and local heat transfer. Model experiments, using Plexiglas plates heated from beneath by water of 50°C, and cooled on the upper side by an air current, and a turbulence (of 1.5%) pressured by a hot-wire anemometer, have been helpful in the establishment and interpretation of the "universal" calibration curve.

261. Direct measurements using a fluxmeter device for the determination of the heat flow losses through the walls of glass tank furnaces have been made by J. Delière,[38] for the calculation of an entire thermal balance diagram. The integral part of the fluxmeter is an adequate system of Constantan alloy thermocouples in series, coiled on a refractory frame, sandwiched between plates fixed on the exterior walls of the tank in an optimum-efficient position. The wires of the thermocouples assemblies may also consist of a more stable alloy of silver-constantan, the noble metal being applied on the core of the wires by electrolytic deposition for higher temperatures (above 500°C) and gradients. In special cases, thermocouple combinations of higher electromotoric force may be used. As the principal sources of errors for such thermocouple fluxmeters, Delière studied effects of variable rugosity of the wall refractories, and their heat radiation emission.

262. For the temperature range from 300° to 900°C, important progress has been made in the development of rapid-indicating radiation pyrometers, indispensable for the near-infrared range from 0.0 to 2.0 μ, working on the principle of photocells (with a maximum spectral sensitivity at 2.5 μ), specifically useful in the case where the emissivity of the sample is not equal to 1.0. The same radiation pyrometer is after N. Neuroth,[39] used for the determination of temperatures in glass melts in a certain depth of the melt bath and specifically useful for temperature controls over the surface temperature of glass during blowing and shaping dies. The indication of such instruments, based on the principle of lead sulfide resistance cells must be corrected by averaging. The instrument is generally not recommended for measurements of glass sheets, however, with only a slight modification, it is well suited for measurements of the temperatures on glass surfaces when the infrared radiation is applied over the range from 5 to 7.5 μ, e.g., when a photocell (of a maximum sensitivity at 6.5 μ) is built in, replacing the lead sulfide cell, e.g., by one on the basis of InSb.

263. W. Weiss[40] analyzed the influence of a *staining* component added to the composition of a normally colorless industrial glass and its cooling rate, as indicated

[38] *Silicates ind.* **30**, (5), 233–242 (1965).
[39] *Glastech. Ber.* **39**, (3), 197–200 (1961).
[40] *Glastech. Ber.* **37**, (12), 553–562 (1964); *Tech.-Wiss. Abh. Osram-Ges.* **9**, 225–240 (1967).

by the total emissivity. The viscosity of such glasses was controlled at the same time over a defined temperature interval, with a lowest limit of 10^4 P (measured in a rotation viscosimeter working on the torque determination principle) for the transition from the softened to the consolidated state. The friction moment was recorded over an oscillograph to determine the emission behavior during the cooling of glass rods. The glasses applied were stained by additions of Fe_2O_3, Cr_2O_3, CuO, V_2O_5, CoO, NiO, MnO_2 in amounts so small that the viscosity was not markedly changed. An MnO_2 stained glass under this treatment showed an apparently anomalous behavior insofar as the cooling time is increased in contrast with normally shorter periods after the addition of the colorant oxides and an increased emission intensity. Such anomalies are explained by a reaction of MnO_2 in the glass with contaminating iron oxides from a considerable reduction of the FeO content. Total emission ϵ_{DT}, can be approximately calculated as well as the percentage shares of radiation, convection, and conductance losses during cooling (e.g., in the viscosity range from 10^4 to 10^8 P).

264. Concerning the optical absorption spectra of iron in rock-forming silicate minerals at room temperature and at 78°K, we refer to extensive measurements made by W. B. White and K. L. Keester,[41] and the critical discussion contributions made by W. H. Turner[42] (cf. ¶ 119 f.) over the range from 400- to 3500-mμ wavelengths. It is essential to realize that those minerals contained divalent Fe^{2+} cations in octahedral $[FeO_6]$ coordination; here the reasons are demonstrated why Turner drastically denied the correctness of White's and Keester's statement that divalent Fe^{2+}ions also would appear in tetrahedral coordination $[Fe^{(II)}O_4]$. The central point in the differences in opinion between those authors is seen in different aspects in application of the ligand-field-model theory (cf. Vol. VII. ¶ 673 ff.) so strongly defended by White and Keester. We come back to such problems in connection with other questions arising in the investigation of ordinary bottle glass coloring effects and the pleochroism of iron silicate minerals over the spectral range from 7000^{-1} and 30,000 cm^{-1}, and their absorption spectra from the visible to the infrared, as discussed by G. H. Faye, P. G. Manning, and E. H. Nickel[43] (cf. VII. ¶ 701).

265. Mention should not be omitted here that considerable advantages in the efficiency of glass melting furnaces may be achieved if one would use the larger scale kiln units of shaft type for which E. Szöke[44] gave construction details and a brief discussion of the superior heat economy of such a type which, in addition, may easily be entirely automated in the furnace conduction.

[41] *Amer. Mineral.* **51**, (5/6), 774–791 (1966).

[42] *Amer. Mineral* **52**, (3/4), 555–558 (1967) (cf. VII. ¶ 699 f.)

[43] See *Amer. Mineral.* **53**, (7/8), 1174–1201 (1968).

[44] Proc. Conf. Silicate Industry, 9th, *SILICONF*, Number 8, pp. 507–513, Akademiai Kiadó Budapest 1967.

266. Concerning a recent attempt to control glass furnace tanks by a regularly repeated survey of the viscosity of the glass melt flowing in the forehearth and in the feeder channels, W. Weiss[45] recommended a simplified measuring technique adapted to robust conditions of practice. The technique can give, in every case important information on more or less considerable fluctuation in the homogeneity of the glass melt running to the feeders, can survey the uniformity of the production of shapes from the machines, like tube drawing, and can establish, from case to case, standard limits of permissible fluctuations in viscosity properties, as determined by a simplified rotation viscosimeter (with a sphere-shaped central stirrer), directly introduced into the feeder opening of the Danner tube device. Normally, the glass will have a viscosity of between 1000 to 1500 P, in order to be stabilized $\pm$ 2 P as currently surveyed in a statistical evaluation. On similar favorable practical experience, the Russian written special literature is rich.[46]

267. The heat conductance of glass melts up to 1400°C was tested by M. Bré and P. Kermabon[47] with the result that an iron (divalent) content in common glass qualities of only 0.1% markedly modifies its physical properties above 900°C. At 1000°C the conductance in a FeO-containing glass is only 0.05, in the same glass entirely free from iron, it is 0.14. When the FeO content is increased, the conductance remains about constant. The thermal conductivity is also reduced by staining with MnO or Cr_2O_3. From 1100° to 1500°C, a rapid increase of the global diffusivity value h is observed. It may be rather general fact that most industrial glasses of blue, green, or neutral-opaline staining have a maximum thermal conductance over the range of 1300° to 1400°C. On the theory of heat energy flow in glass tank baths as a function of heat conductance, see the older publications by M. Czerny;[48] also see for the fundamental correlation between heat conductance and radiation conductance (global diffusivity) $[h_r = (\lambda_c + \lambda_r)/C_p)$, in its importance for the properties of infrared absorbing metal ions (chiefly interesting Fe, Mn, Cr) which is discussed by F. J. Grove and P. E. Jellyman.[49] On the physical background of radiative heat transport in hot glass, we emphasize the valuable bibliography presented by E. U. Condon.[50]

268. Heat transfer by flame luminosity (emissivity) in the glass tank combustion chamber has been theoretically discussed extensively by G. Datschefski;[51]

[45] *Glastech. Ber.* **41**, (1), 13–19 (1968).

[46] Cf. M. V. Okhotin, E. I. Vilenskaya, and A. I. Tusikov, *Steklo Keram.* **19**, (5), 12–14 (1962); M. S. Kazanskiĭ, *Stekolnaya Prom.* **14**, (10), 27–29 (1938); K. G. Kumanin, *ibid.* **15**, (1), 19–21 (1939).

[47] *Verres Refract.* **23**, (1), 3–9 (1969).

[48] *Glastech. Ber.* **25**, (12), 387–392 (1952); Vol. II.B. ¶ 109 ff.

[49] *J. Soc. Glass Technol.* **39**, 9–15T (1955).

[50] *J. Quant. Spectry. Radiative Transfer* **8**, (1), 369–385 (1968).

[51] *Glass Technol.* **10**, (4), 107–113 (1969).

specifically, for the practical application of natural gas which is known to be intrinsically a "semiluminous" fuel. The purely mathematical treatment of the problems involved, and its application for an industrial tank furnace (in a one-port section), shows convincingly that the amount of radiation which is resorbed by the glass bath is not essentially affected by the emissivity of the semiluminous character of the gas flame leaving the side-port burner in a highly turbulent diffusion flame. Yet, G. Datschefski[52] had earlier demonstrated a comparison of the thermal efficiencies of an oil fuel, and a natural gas-fed furnace to show that the latter is 4% more efficient than the heavy oil firing in its thermal output. This agrees with the experience of M. H. de Lange,[53] although the European fuel oil used had a much higher nitrogen content than the American oil used by Datschefski.

269. After a brief review of cooperative interaction phenomena between heat conductance and heat radiation, Gr. H. Chui and R. Gardon[54] presented a discussion of the one-dimensional factors of quality of heat contacts and the reflectivity and thickness of the materials used for the measurements of total absorption parameters. The principal results of a computer-controlled calculation of these complex physical problems is that both actions exhibit a distinct mutual influence on one another. For the conditions existing in a glass tank furnace, one must consider that flames and heat transfer from the roofs act by radiation onto the glass bath, but that its transmissivity is often rather subordinate to one or the other range of radiation wavelengths. The glass bath in its thin-surface layers, absorbs the radiated heat and the ensuing heat transfer must have predominantly the character of convection.[55]

270 A steady-state mathematical model for the calculation of temperature profiles and heat-transfer conditions in flowing glass baths was developed by J. H. Duffin,[56] with particular details for conditions in forehearth channels. The model equations were then reexamined for the numerical correlations by integration over a programmed system for high-speed digital computers, the results of which are promising a great deal for a thorough application for operation control, also for an optimum design of forehearths, as demonstrated by practice with different types of glasses, including flint and dark green.[57]

271. An important contribution to measurement data of the total emission de-

[52] *Glass Technol.* **8**, (6), 148–153 (1967).

[53] *Glastech. Ber.* **40**, (9), 337–344 (1967); and H. Buschmann, *ibid.* **38**, (3), 86–92 (1965).

[54] *J. Amer. Ceram. Soc.* **52**, (10), 548–553 (1969).

[55] Cf. W. Trier, *Glastech. Ber.* **26**, (1), 5–12 (1953).

[56] *Bull. Amer. Ceram. Soc.* **49**, (2), 180–187 (1970).

[57] Cf. F. H. Finger, Report to Glass Container Industry Research Corporation, 1966, based on material from about forty different runs.

grees of glasses and sintered oxides over a temperature range from −60° to +250°C in their functional correlation to temperature, and the angle of incidence, was made by J. Lohrengel.[58] The total emission degree $\epsilon = f(T, \theta)$, as a surface quality dependent constant, is defined by the ratio of the radiation density in a definite direction, for the given sample of the radiator, to the radiation density of the black body of the same temperature. The black body chosen had an inner surface coating of CoO, and an apparent emission degree lying between 0.9990 to 0.9999, (0.985 determined as the effective value for 60°C). Lohrengel examined different samples of different industrial glasses for their emission behavior at 100°C in comparison with silica glass, and different sintered oxide bodies. Among the latter, alumina is particularly strongly influenced by small additions of Cr_2O_3 in the emission degree, whereas, for common window glasses, no essential differences caused by variable compositions or by diversities in the production methods could be detected.

272. It is highly interesting that M. J. Austin[59] could recently develop a satisfactory mathematical simulation of the working conditions for an all-electric glass melting furnace which is applicable for studies of the effects of batch thickness and the exterior temperatures of the glass in combination with purely mechanical-technological factors like the pull, power input, and the color of the glass and its durability. Omitting here the purely operational variables like the pull, the model indicates for glasses with a high absorption coefficient in the near-infrared (i.e., amber or green colored glasses), larger thickness data for the batch build-up than those derived for colorless glasses, under the same exterior conditions. All this is in satisfactory agreement with the predictions of the model concept, and practical experience and observations. These calculations are supplemented by calculations of the heat transport in the model, by bulk conduction, and heat transfer.

Finally, we briefly refer to calculations of the temperature profiles in the continuous glass fiber spinning processes, examined by a two-dimensional analysis as given by G. Manfrè.[60]

AMBER GLASS

273. In certain respects, the so-called "amber glasses" are a rather particular class of industrial products, often but not very accurately called "coal-brown", for which blast furnace slags are a cheap and abundant raw material which, by their

[58] *Glastech. Ber.* **43**, (12), 493–500 (1970); cf. VII. ¶ 474.
[59] *Glass Technol.* **11**, (5), 128–134 (1970).
[60] *Verres Refract.* **26**, (2), 57–65 (1972).

contents of sulfides of calcium, manganese, a.o. (cf. Vol. II.C. ¶ 12, 47, 108) have not only a reducing influence on the batch reactions of bottle glass production, but show an intense staining by dispersoids of FeS (cf. Vol. VI.C. ¶ 142).[61] D. Brown and R. W. Douglas[62] presented a detailed investigation of the fundamental reactions in the evolution of the brown color pigments in amber glass in which the role of carbon, together with the partial pressure effects of the furnace atmosphere, with oxygen and sulfur dioxide is of significance to the possibilities of establishing gas reactions in the melting and fining glass. Oxygen partial pressures between 10^{-8} to 10^{-10} atm are ruling in such atmospheres for a glass containing 0.1% Fe_2O_3, in equilibrium with a partial pressure of sulfur above 10^{-2} atm.

274. The importance of the oxygen anion activity for the retention of sulfur in the glass melts was studied by Brown and Douglas who demonstrated quantitatively for all of the industrially interesting concentrations and optimum temperatures, the conditions for a reproduction of quasiequilibrium, and therewith established reliable reproducibility for amber-glass manufacturing. Nevertheless, it is probably not too self-evident that one must expressly be warned against a definition that amber-brown color properties are an evidence for a real coal-staining effect, as such, since the chemical reactions during cooling the presence of coal in the batch mixture are indispensable for maintaining a reducing gas medium during the melting and fining periods to stabilize the redox conditions. The specific merit of the investigations made by Brown and Douglas is seen in their extensive studies using spectroscopic methods in combination with chemical-analytical determinations to interpret the influence of glass composition of a successful conduction of the technological process, e.g., in common alkali-calcium silicate and sodium aluminosilicate glasses, finally in "Cabal" type (calcium boroaluminate) glasses. In principle, the only purpose of an industrially applied addition of iron and chromium oxides to such glass compositions is to regulate and control the redox conditions to maintain production of an entirely uniform material.

275. Industrially highly important also are abundant data and diagrams in the publications by Brown and Douglas showing the influence of variant fusion time periods in the evolution of the color intensity as it is shown, e.g., in Fig. 77, for the transmission curves of a typical Cabal glass (with 48% CaO; 15% Al_2O_3; 37% B_2O_3), and the effects of variable iron contents (analytically determined as Fe_2O_3) for a simple sodium silicate glass (with 25 mole % Na_2O; 75 mole % SiO_2) with varying additions of 0.047, 0.0044, and 0.010% Fe_2O_3, respectively (Fig. 78).

[61] On the economic importance of blast furnace slags as a bottle glass raw material, see the report by R. Persson, *Glass Ind.* **47**, (10), 537–539 (1966); **47**, (10), 583–584 (1966). (see II.B. ¶ 36, 87).

[62] *Glass Technol.* **6**, (6), 190–196 (1965).

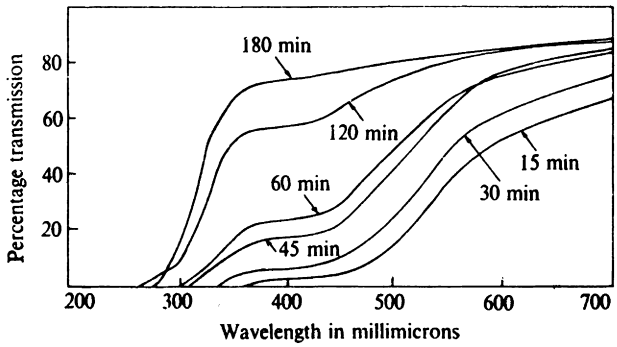


FIG. 77. Transmission curves for various times of melting of glass 48% CaO, 15% Al_2O_3, 37% B_2O_3. (Brown and Douglas.)

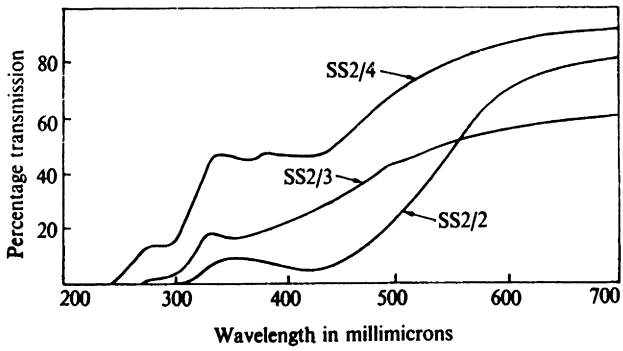


FIG. 78. Effects of the iron contents (in % Fe_2O_3, from analytical data) of different samples of the glass 25% Na_2O, 75% SiO_2 on the percentage transmission. (Brown and Douglas.) Glass SS2/2 contained 0.043% Fe_2O_3; Glass SS2/3: 0.0044%; Glass SS2/4: 0.010%. Thicknesses of the samples were 1.03, 2.45, 0.86 mm, respectively.

276. It is perhaps not necessary to emphasize here the high importance of the ultraviolet absorption and spectroscopic analysis of typical amber glasses not only from the viewpoints of the hygienics and everyday use of containers for radiation-sensitive nutrients, food, beverages, and the like, but to also fulfill important requirements for highly sensitive pharmaceutical products like vitamins, alkaloids, etc. Food and beverages like beer and wine, require amber from the mass production of bottles, and must be guaranteed full protection against obnoxious radiation. Ultraviolet radiation of wavelength near 300 mμ is here of particular concern. We may emphasize that V. Gottardi[63] considered that the "obnoxious" radiations should be

[63] *Ind. Agr.* **5**, ottobre, 551–554 (1967); Conf. Int. Congr. Glass, 1967, Congresso sui Contenitori per Vino, Asti, 1968, pp. 39–48.

extended into the visible ranges, e.g., to 560 mμ for perishable beverages, so much the more so as M. Kriz and J. Krivanek[64] demonstrated distinct changes in nutritious oils and pharmaceutical preparations by radiation transmitted by container glasses between 430 and 400 mμ. The publications by Gottardi are particularly valuable for having spectroscopic diagrams which show the strong absorption of additions of iron and chromium oxides in common bottle glasses, but above all of typical amber glasses which have a practically complete extinction from 300 to 480 mμ, followed by a rather steep increase of transmissivity to a maximum near 650 mμ, and a rather smooth decrease again between 650 and 900 mμ.[65]

277. In this connection, interesting absorption spectrographic investigations of glasses containing tetravalent chromium, Cr^{4+} (e.g., in concentration of only 0.02 wt %), in glass were made by S. P. Lunkin, D. G. Galimova, and D. M. Yudin[66] of bluish tint, and an absorption maximum at 610 mμ. Another interesting study was made by K. Karlsson[67] on iron-containing amber glass on the basis of a ratio Na_2O: $SiO_3 = 3:7$, in which Fe_2O_3 was reduced to FeO by an admixture of sugar to the glass batch. The presence of Fe^{2+} ions is evident in the near infrared by the absorption band of 9500 cm^{-1}, Fe^{3+} by bands at 11,900 and 15,400 cm^{-1} corresponding to a complex in octahedral coordination. Another band at 24,300 cm^{-1} is interpreted by Karlsson as indicating the tetrahedral $[Fe^{III}O_4]$ group; characteristic for the reduced state is another tetrahedral group, in which S atoms replace oxygen sites.

278. Much more detailed observations on the production of brown and amber glass starting from FeS_2 (as the mineral pyrite) in the batch mixture, were contributed by H. Claus.[68] This author started with the idea that the color intensity of $NaFeS_2$ as a constituent may be superior to the common pigmentation of amber glasses, and may have a desirable influence on the suppression of gas bubble evolution in the fining process, when no sulfate is present in both the glass mixture and the early melts. The role of carbon (commonly introduced as coal powder) in combination with pyrite is to develop optimum color intensity and a good fining behavior when, empirically, mixtures with 0.06 to 1.14% coal and 0.12 to 0.16% pyrite are charged. When coal is *not* added to the batch composition, the pyrite can bring about a good amber staining effect only in a reducing atmosphere, and the admixture of pyrite must be raised by 0.4 to 0.5%, but higher additions of FeS_2 make the glass reddish-

[64] *Silikaty* **3**, 215–230 (1963).

[65] See also G. Paoletti, *Riv. Birra Vino* **14**, (7), 3–7 (1967), with experimental data on amber glass spectroscopy, and projections in the tricoloric Maxwell–Helmholtz color diagram.

[66] *Opt. Spectrosk.* **25**, (4), 323 f., (1968) (Eng. transl.: *Opt. Spectry.*).

[67] *Glastek. Tidskr.* **24**, (4), 13–19 (1969).

[68] *Tonind.-Z.* **92**, (12), 501–503 (1968).

brown or even black to opacity. It is important to note that coal alone never makes industrially serviceable amber staining possible. In the best case, there is a slight yellow tint from traces of sulfur in the coal in the presence of iron and in glass sand. Claus also described reactions of elementary sulfur with iron oxides which bring about good amber staining effects.

279. P. Emer[69] mentions that amber glass is commonly molten in industry in an oxidizing gas atmosphere, i.e., with a formation of some sulfate simultaneously with sulfide and other deviations from the ideal process. Analogous to amber glass containing iron as the indispensable staining element, T. I. Veĭnberg and N. I. Grebenshchikov[70] described interesting sulfide-stained varieties in which sulfides of indium, gallium, germanium, thallium, bismuth, and lead are essential pigments. On this basis, it may be possible to produce specifically modified sulfide-stained glasses which may be useful as radiation filters in the near infrared.

280. Coming back to the principle of amber-glass staining methods, it is interesting to see that M. S. Zaman and A. Paul[71] proposed a rapid method for an estimation of redox ions in such dispersoid systems (cf. Vol. II.C. ¶ 98; Vol. VI. C. ¶ 142) analytically to determine divalent and trivalent iron, sulfide, and sulfate, S, in brown colored glasses, from the maximum optical density in the near infrared (1 λ wavelength); the divalent iron, divalent sulfur (the total reducing matter) by titration with ICI, the total iron by titration with thioglycolic acid (cf. ¶ 113, 208).

SELECTIVITY OF TRANSMISSIVITY AND REFLECTANCE OF SPECIAL GLASS

281. For the general use of optical pyrometers in glass plant operation and the importance of the heat radiation and transfer indicated in glass furnaces, in particular, F. Cabannes[72] interprets the basic physical principles and theoretical backgrounds. Special emphasis is given to *selectivity* phenomena as characterized by the spectral reflectance indicatrix over the visible and medium-long infrared ranges. Refractories of the wall construction of glass furnaces may be characterized for the wavelengths of 5 to 6 μ near to the conditions of the black body radiator; the glass surface appears opaque in this range. With the Land pseudomonochromatic pyrometer it is possible to measure the surface temperatures rather well (for 1- to 11-μ wavelengths), but the influence of water-vapor absorption must be considered;

[69] In a review of Claus' experimental results, *Glastech. Ber.* **43**, (10), 426 (1970).
[70] *Zh. Prikl. Khim.* **42**, (6), 1266–1270 (1969).
[71] *Glass Technol.* **10**, (4), 93–98 (1969).
[72] *Silicate Ind.* **29**, (12), 501–509 (1964).

particularly well suited for glass plant use and surface temperature control is the total radiation pyrometer of D. F. Kelsall[73] which contains a lead sulfide photocell as the radiation-sensitive unit.

282. A. S. Grenis and A. P. Levitt[74] describe a special device for radiation measurements of refractories which are of basic importance for the heat household in glass tank furnaces (as spoken of in ¶ 261), and of flame-sprayed coatings of refractory oxides like Al_2O_3, Cr_2O_3, ZrO_2, and BN by their specific emission properties over the range from 1 to 10 μ, at 1300°K, also in their functional correlation to rugosity qualities of the refractories in question. In general, the total emission of alumina and zirconia is somewhat below that of the black body, with a maximum of emission intensity at about the same wavelength. Chromium oxide most approximates black-body-like emission characteristics, whereas boron nitride markedly deviates from blackbody conditions.

283. The problem of the presence of divalent iron as determined by optical spectroscopy, chiefly by the near-infrared band of 1050 mμ, with an extinction coefficient, ϵ, of 28.9 liter mole^{-1} cm^{-1} for a Na silicate glass (ratio $Na_2O/SiO_2 = 3:7$); and a Na borate glass (with $Na_2O:B_2O_3 = 1:9$), both at 980 mμ, was examined anew by F. N. Steele and R. W. Douglas.[75] In both cases, the coordination was octahedral for divalent Fe atoms. The Na silicate glass, however, also indicated three additional bands at 380, 430, and 440 mμ which correspond to trivalent Fe in tetrahedral coordination. These were absent from the borate glass. In the ultraviolet range, strong absorption at 230 mμ with the high extinction coefficient of $\epsilon = 7000$, indicates the steep cutoff edge by the strong ferric charge-transfer effect and the low-energy "tail" of the band (according to a rule of W. Urbach), and corresponds to the electron transition reaction in divalent iron (see Fig. 79). The same reaction in trivalent iron is indicated in the borate glasses by a considerably wider band of approximately the same intensity. In the ultraviolet range also, divalent iron brings about an absorption band caused by electron transitions, namely for the silicate glasses at 210 mμ with $\epsilon = 3000$. It is, however, difficult to give more precise data by the eigenabsorption of the base glass in the range here concerned. Highly instructive for a comparison between the conditions of absorption in silicate and borate glasses of this kind is another comparison between solutions of ferric and ferrous ammounium sulfates, namely, of $NH_4Fe^{III}(SO_4)_2 \cdot 12H_2O$ (in concentration of only 0.0001 mole) and $(NH_4)_2Fe^{II}(SO_4)_2 \cdot 6H_2O$ (concentration 0.025 molar), both in $2n$ H_2SO_4 (cf. Fig. 80).

284. Divalent iron silicate glasses, with their strong absorption in the near infra-

[73] *J. Sci. Instr.* **40**, (1) 1–4 (1963).
[74] *Bull. Amer. Ceram. Soc.* **44**, (11), 901–906 (1965).
[75] *Phys. Chem. Glasses*, **6**, (6), 246–252 (1965).

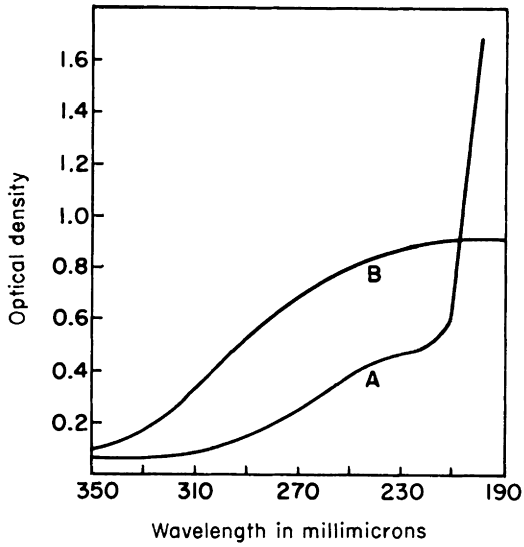


FIG. 79. Optical density vs. wavelength over the range from 350 to 190 mμ, for the silicate glass (A) $3Na_2O$, $7SiO_2$, containing 0.0415 wt.% Fe_2O_3; and the borate glass (B) Na_2O, $9B_2O_3$, containing 0.021 wt.% Fe_2O_3. Sample thickness 0.072 and 3.43 mm, respectively. (Steele and Douglas.)

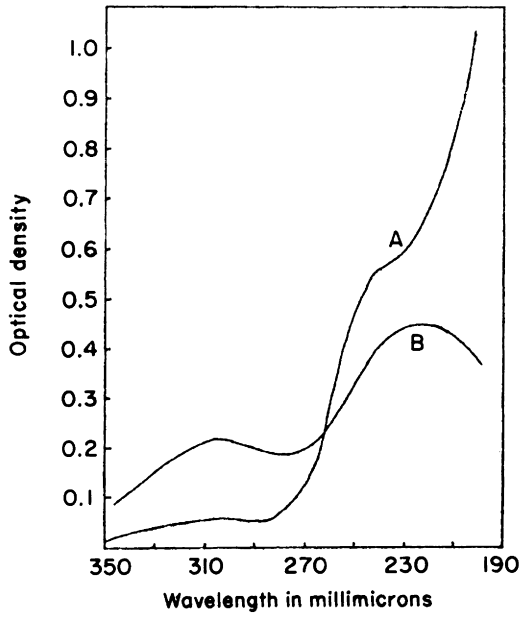


FIG. 80. Optical density vs. wavelength for ferrous and ferric ammonium sulfate solutions over the range from 350 to 190 mμ. (Steele and Douglas.) (A) 0.0001 *M* solution of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in *2n* H_2SO_4. (B) 0.025 *M* solution of $Fe(NH_4)_2(SO_4) \cdot 6H_2O$ in *2n* H_2SO_4.

red, have been often discussed as possibilities for reducing entrance of undesirable sun radiation into modern houses through special window glass combinations. In such arrangements, the absorption of the window glass must go hand in hand with an *increased reflectance* to bar undesirable heat from the rooms just on the threshold, when it would be economically tolerable to apply thin coatings of metal oxides, or dielectrics, on the radiation-absorbing glass surface to increase the reflectance of the system glass-plus-coating layer.

285. Modification of their heat-absorbing capacity is an important problem with many commercial glasses used for *shielding* against incident sunlight in commercial buildings and residences especially to reduce the intensity of transmitted ultraviolet and infrared radiation. H. Schröder[76] solved this problem by the elegant method of applying onto the glass surface a thin film (thickness about $\frac{1}{2}$ to $\frac{1}{4}$ of the wavelength of visible light) of an antireflecting solid compound, preferably silica or titania, as precipitated from organic complex compounds like esters of silicic or titanic acid. In the place of these oxides, one may apply very thin metal films (preferably gold) onto window glass by a high-vacuum deposition; such films show an increased reflectance for infrared radiation, while transmission of visible light is little affected. For applying silica or titania films, one may dip the glass in liquid esters (pure or mixed), or apply alternating layers onto the glass of good adhesion and uniformity in thickness. Organosilicates or titanates are either hydrolyzed or pyrolyzed by a subsequent special treatment. The methods here recommended by Schröder open many ways and means that are attractive for their high reproducibility and possibilities of varying and directing the selective reflectance of those films in the ultraviolet or infrared. A multiplicity of diversified modifications can achieve sunlight damping effects down to only 5% of the initial radiation intensity, by selecting films of a stepwise variation in the refractive indices of the medium (1.44 for silica; 1.77 for ZrO_2; 2.20 for titania) in three to six layers, one above the other.[77]

286. H. Schröder[78] described the physical premises which must be fulfilled for the success of such a mechanism; selective reflection of radiation from sunlight must be raised to the desired degree without any unfavorable effect on optical transmission. Coatings of this kind can be applied relatively easily, either by spraying *in vacuo*, or by adequate dipping in reagent solutions in the chemical way. Coatings with metals of high efficiency in this direction could be of gold or such dielectric material as binary mixes of oxides, preferably titanates, as semiconductors. Combin-

[76] *Verres Refract.* **18**, (2), 89–97 (1964); with many instructive transmission spectra diagrams from practical applications; *Opt. Acta.* **9**, 249 ff. (1962).

[77] See also H. Bach, *Naturwissenschaften* **51**, (1), 10 f. (1964) (cf. VII. ¶ 943).

[78] *Vetro Silicati* **10**, (60), (6), 10–14 (1966), with valuable bibliography also of patent literature.

ations of such layers also offer possible solutions to the problems involved. It is by no means excluded that one day even *phototropic* materials can be used for sun-shielding entire buildings, halls, auditoriums, markets, and the like.[79] As instructive examples of the characteristics of special glass composities with coatings, Fig. 81 shows a spectral diagram for the effect of triple layers of $TiO_2/SiO_2/TiO_2$, and Fig. 82, another combination with $TiO_2/CoO_n/TiO_2$. The latter composite shows a total transmission of 35% of the incident sun radiation and a reflectance up to 30.5%.

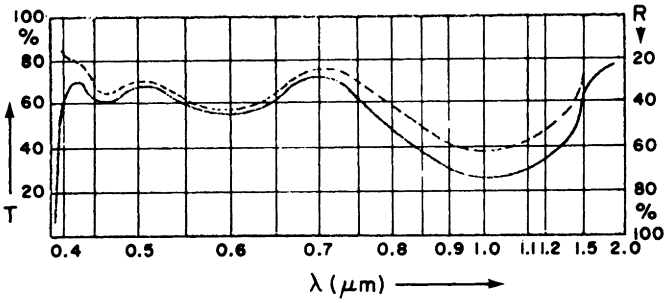


FIG. 81. Single pane coated with triple layer $TiO_2/SiO_2/TiO_2$. (Schroeder.)

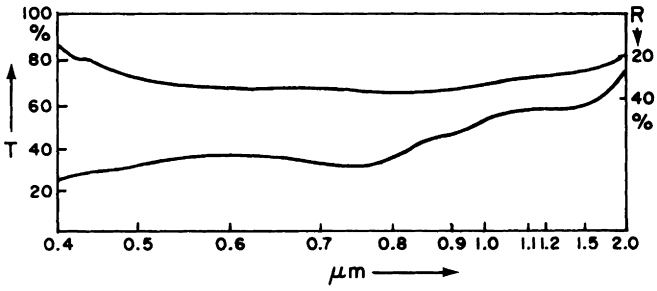


FIG. 82. Single pane coated with triple layer $TiO_2/CoO_x/TiO_2$. (Schroeder.)

[79] Cf. Vol. VII. ¶ 781 ff. on phototropic glass.

Part B: Physical Properties of Glass as a Function of the Chemical Composition

THE PRINCIPLE OF ADDITIVITY

287. Starting in 1894 with the classical publications of A. Winkelmann and O. Schott, on their successful systematic studies of thermal durability, the modulus of elasticity, compressive, and tensile strength of different types of glasses of the Jena Glass Works, there is up to the present date, one uniform tendency to find fundamentally and universally valid functional correlations between the physical properties of practically important glasses and their chemical composition. Development of functional equation systems of the simplest form were sought for these correlations; the ideal solution would be linear equations of additive regularities, from case to case. In principle, not too much has changed so far; modern authors continue to drive.

288. Among many examples are the excellent results presented by C. J. Phillips,[80] on new calculation methods for the Young (elasticity) modulus, from the mole percent composition of both simple and highly complex silicate glasses. Phillips also speaks of individually characteristic "increments" for one of the glass-forming oxides which may be true material constants; he emphasizes, however, that this expectation is only partially fulfilled for silica, alumina, and calcium oxide. The situation is already somewhat more complicated for the alkalies and lead oxide, the increments of which are systematically variant with the total content of glass "formers" in the given samples. Boron trioxide, and the alkalies have increments (coefficients, as Phillips calls them) which are directly proportional to the summary shares in alkalies, R_2O, and also depend on the ratio $(R_2O - Al_2O_3) : B_2O_3$ in the molar composition, whereas, MgO, BaO, and ZnO are directly related to the alkali contents of the glasses concerned.

289. Nevertheless, it is permissible schematically to write the fundamental law for the Young elasticity modulus in simplest additive relations to the mole percentage composition variables, to achieve a practically satisfactory agreement between the calculated, experimental, and theoretical data with deviations of $\pm 0.3\%$ of the results, i.e., with an approximation of observation to theory which is roughly by one order of magnitude better than that determined in previous attempts to master the prob-

[80] *Glass Technol* **5**, (12), 216–223 (1964).

lems.[81] The calculations by Phillips do not cover any possibility for reaching simple (linear) additivity since many of the increments vary with $SiO_2 + Al_2O_3$, and as a function of B_2O_3, others with R_2O, and one for B_2O_3, even with the ratio (alkalies – Al_2O_3): B_2O_3, *and* with R_2O. A drastic (precipitous) drop in the increment for BaO cannot be simply introduced into calculations, nor can a rapid rise in that of ZnO near 8 mole % R_2O.

290. Later, C. J. Phillips,[82] after a continued evaluation of his results concerning the mechanism of the compressive strength of glass, came to the conclusion that it is not so much the number of broken bonds, Si – O – Si per cm^3 that determines the strength of a given glass, but that the elasticity modulus is the decisive factor. Several commercial glasses may show a directly linear functional correlation between fracture strength and the modulus of elasticity, independent of a previous surface treatment. This phenomenon may be understood by the elementary assumption that the number of surface defects (flaws) is inversely proportional to the modulus of elasticity.

291. Another attempt at an interpretation of correlations existing between the chemical composition of no fewer than 156 selected samples and of ceramic *glazes* of the polynary system $Na_2O - CaO - PbO - Al_2O_3 - B_2O_3 - SiO_2$, was made by G. J. Roberts, S. Salt, W. Roberts, and C. E. L. Franklin,[83] not only by examination of the Young modulus, but also by a comparison with density, thermal expansion coefficient, microhardness (as measured by a simplified "scratch" test), refractive index, and flow properties. Since we will come back to these experiments in connection with the technological behavior of ceramic glazes and enamels, we may here only briefly establish that no principal difference exists between glasses and glazes and that, with a certain critical precaution, of course, the expected correlations for those classes may be rather liberally applied with satisfactory results.

292. Coming back to a theoretical consideration of fundamental glass properties in functional combination with glass composition, and more practically that for glass constitution effects, T. Moriya[84] applied his "microphase" or "micellae" theory (cf. Vol. II.A. ¶ 306; Vol. VII. ¶ 805) which specifically was to respond to viscoelastic properties at temperatures near the transformation point (also the annealing temperatures) and to changes in the refractive index near the softening range. An approximate calculation of parameters for selected glass properties from the molar chemical composition is also thinkable here with some satisfactory succes, from

[81] Cf. E. I. Kozlovskaya, Proc. All-Union Conf. on Glassy State, 3rd, Leningrad, 1959 (Eng. transl. pp. 299–301, Consultants Bur., New York, 1960; cf. II.B. ¶ 125, Footnote 197.

[82] Compt. rend. Congr. Int. du Verre, Bruxelles, June/July, 1965, published 1966, III. 1/95, 1–7.

[83] Trans. Brit. Ceram. Soc. **63**, (10), 553–902 (1964); cf. II.B. ¶ 264, Footnote 427; VIII. ¶ 462, 508.

[84] Bull. Tokyo Inst. of Technol., 1965, March (66), pp. 29–79.

increments for the oxidic ingredients, with respect to the sizes of "microphases" (micellar domains) for the thermal expansion coefficient, the molar refraction, and even for the water leaching intensity, not to speak of some electric properties. The micellar theory, however, is particularly useful for studies of transitions from micellar theory, however, is particularly useful for studies of transitions from micellae, to nucleation centers and crystallization phenomena.[85]

293. Much deeper-going problems of the influence of glass constitution on the physical properties of glasses are discussed by R. Brückner and J. F. Navarro[86] in the simple binary system $B_2O_3-SiO_2$, over the range from 2 to 60 mole % SiO_2, the viscosity between 300° and 1100°C, the thermal expansion coefficient up to the softening range, and in the "frozen-in" state, the molecular volume, the infrared spectra, and the solubility in water. From the viscosity as a function of temperature, it is concluded that with increasing concentration of silica, an increasingly higher three-dimensional structural order is established in the framework aggregates (cf. Vol. II.A. ¶ 216 ff., 235 ff.; Vol. VII. ¶ 382) along with an increasing cooperative structural consolidation, and a more uniform dispersity of the components, but constitution changes from a framework with predominant B_2O_3, to another one in which silica is determinative. There is no indication that any binary compound is formed, or that coordination conditions have changed. Nevertheless, there was a strong deviation from a strictly additive character of the thermal expansion coefficient (cf. Fig. 83), another anomaly for the partial volume [V_0 for 20 to 40 mole % SiO_2 (Fig. 84), although tolerably normal for the molar volume V_m] the partial volumes of both oxides, the molar refraction, and the specific refraction as a function of composition.

294. The fact that in glasses of the ternary system $Na_2O-ZnO-SiO_2$ varying greatly in composition, no discontinuities and no sudden changes in the refractive indices, thermal expansion coefficients, molar refraction, density, and inner friction occur, was interpreted by J. C. Hurt,[87] J. C. Hurt, and C. J. Phillips[88] from measurements in glasses of the composition range between 50 and 75 mole % SiO_2 and up to 35 mole % ZnO. When the concentration in ZnO was increased in the same measure, the thermal expansion coefficient decreased in the same measure; density and refractive indexes and activation energy for the diffusion of Na^+ ions also increased. From the infrared spectra in the range from 1500 to 70 cm^{-1} the presence of $[ZnO_6]$ and $[ZnO_4]$ groups side by side could be established. The infrared spectroscopic method proved here to be an excellent tool for direct observation of

[85] For the theory of glass-ceramics in their technological evolution (cf. III.A. ¶ 39).

[86] *Glastech. Ber.* **39**, (6), 283–293 (1966).

[87] *Diss. Abstr. B* **28**, (5), 1914 (1967).

[88] *J. Amer. Ceram. Soc.* **53**, (5), 269–273 (1970).

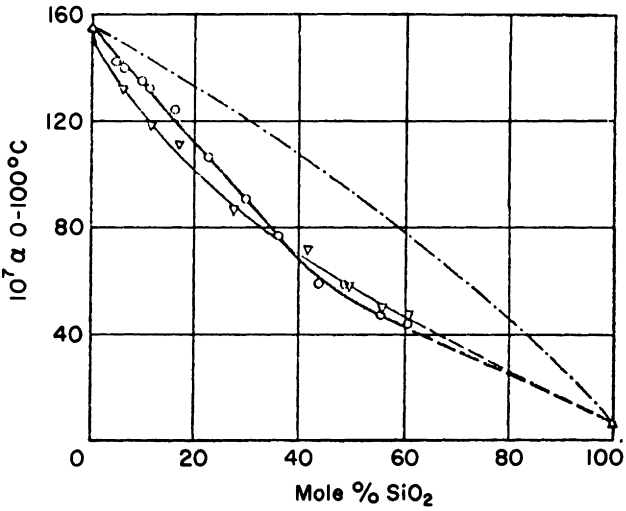


FIG. 83. Thermal expansion coefficient (between 0° and 100°C) of $B_2O_3-SiO_2$ glasses as a function of the mole % SiO_2 contents. (Brückner and Navarro.) ○, after measurements of the authors; ▽, after Cousen and Turner, 1928; dash-line corresponds to ideal-additive behavior of the glasses.

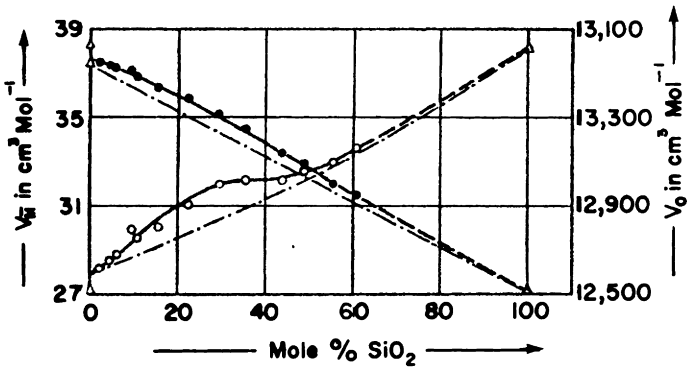


FIG. 84. Mole volume and oxygen partial volume as functions of the contents in SiO_2. (Brückner and Navarro.) Dash lines correspond to additivity conditions; the curves to measurement data; ○ to $V_M = M/\rho$; ○ to $V_M/(3x_1 + 2x_2)$ = the partial oxygen volume (V_0).

the ligancy of Zn^{2+} in the constitution of silicate glasses.[89] The remarkably smooth character of the changes in the physical property parameters as a function of composition is discussed as a consequence of the polarizability of the Zn^{2+} cations. The

[89] Cf. P. Tarte, in the Proc. Internatl. Confer. on "Physics of Non-Crystalline Solids" (J. Prins, ed.), Delft 1964, pp. 549–565, North Holland Publshg. Comp., Amsterdam, 1964, pbl. 1965; *Spectrochim. Acta.* **18**, (4), 467–483 (1962).

increases in the activation energy for the diffusion of Na^+ ions, as mentioned above, speak against a hypothesis postulating that with increasing presence of ZnO, the free mobility fact and diffusion of Na^+ would be promoted and accelerated; that was not observed. The theory of "nontouching" oxygen atoms was also not confirmed in the same connection. That $[ZnO_4]$ groups are present is made essentially convincing by the shifting of the infrared band from 600 to 400 cm^{-1}, i.e., to higher frequencies, $[ZnO_6]$ groups are simultaneously indicated by absorption bands at 300 to 100 cm^{-1}.

295. W. Poch[90] used the variability of chemical composition for general studies of constitution and changes in the properties of glasses of the simple binary system $NaF-B_2O_3$. The aim was to derive functional correlations to the composition from changes in refractive index, density, thermal expansion coefficient, the transformation and softening temperatures, the infrared to ultraviolet transmission, data of anionic molar volume, and mole refraction. The appearance of $[BO_4]$ bands in the infrared spectrum makes the introduction of F^- ions into the framework structure of such glasses highly probable, i.e., the formation of B—F bonds. The number of the $[BO_4]$ units present increases steadily up to a concentration of 55 mole % NaF, with about 0.7 $[BX_4]$ groups for one F^- anion each. Furthermore, Poch concluded that besides $B-(F)_4$ and $B-(O)_3$ an increasing concentration of NaF in the glasses in different concentration ranges brings about the development of bond types of central B atoms, flanked on both sides with (O) and (F) atoms, as seen from Fig. 85; F^- is prevalent in the $[BX_4]$ groups, but not statistically distributed by a replacement of O^{2-} in oxoborate glasses. These facts make striking a certain analogy of the coordination conditions of the $NaF-B_2O_3$ glasses with those of alkali borate glasses, $R_2O-B_2O_3$. When the concentration in F^- is low, their functional possibilities for bridging, in the place of O^{2-} anions, is restricted, but, when the concentration in NaF is high, the number of possible F bridges may even be predominant, as is the case with alkali borate glasses with B—O—F bonds (somewhat weaker, however), and will show anomalies.

296. In silicate glasses, C. L. Babcock[91] analyzed statistically the correlations between structural properties of simple glasses with their chosen composition as seen from the fields of primary crystallization in the phase equilibrium diagrams of the corresponding systems. It is striking that whenever there are continuous linear-additive parameters for certain tested properties in such fields, points of invariancy and discontinuities may occur abruptly in the refractive indices, the specific volumes, and viscosities, over the temperature range from 1500° to 1260°C. The method of

[90] *Glastech. Ber.* **40**, (7), 261–267 (1967).
[91] *J. Amer. Ceram. Soc.* **51**, 163–169 (1968).

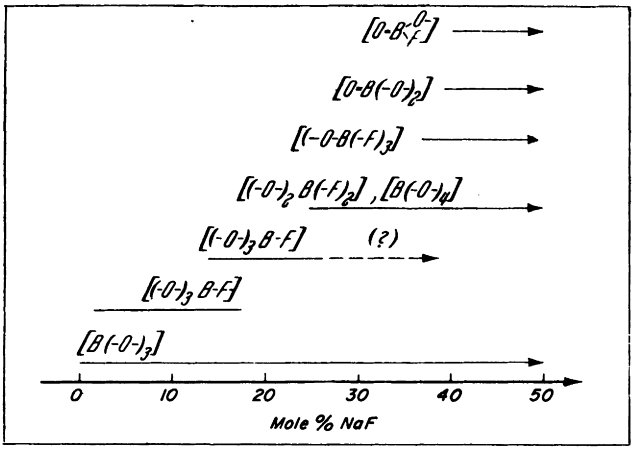


FIG. 85. Schematic representation of different structural units present in NaF containing borate glass compositions over various concentration ranges of NaF. (Poch.)

least-square and smallest errors analysis from an evaluation of 1100 binary, ternary, and quaternary silicate glasses, makes it evident that the discontinuities are best interpreted as indicating "substructures" in which the framework of the normal glass is to be distinguished by microstructures determined by the nature and arrangement of framework-modifying constituents. In solid silicate glasses structural units may then occur which correspond to potential primary crystallization phases; most frequently they may be of the tridymite or cristobalite type normally expected as devitrification products. Babcock[92] illustrated these ideas on "substructures" by "precrystallization" framework arrangements in environmental portions of the phase equilibrium diagrams for a series of Na–Ca silicate glasses in which those primary "quasicrystalline" types are demonstrated:

cristobalite	tridymite	quartz	pseudowollastonite	wollastonite
Na_2SiO_3	$Na_2Si_2O_5$	—	$Na_2O.2CaO.3SiO_3$	$Na_2O.3CaO.6SiO_2$ ("devitrite")

It is to be understood that in the earliest state all these phases are *para*-crystalline, although they are quite similar to their full-crystalline counterparts.

297. Eminently practical purposes are pursued by O. Knapp[93] in studies of the chemical composition of glass used for champagne bottles which must be guaranteed to be safe from fracturing under internal pressures. The inner pressures may appear as a sudden increase (shock) in hydrostatic pressure, or as a fatigue phenomenon

[92] *J. Amer. Ceram. Soc.* **52**, (3), 151–153 (1969).
[93] *Silikattechnik* **18**, (11), 358–359 (1967).

during long service. When the mechanical strength resistance, F_m—as a function of the modulus of elasticity, E, and the tensile strength, P,—is given by the well-known equation $F_m = P/\alpha E$ (α the coefficient of thermal expansion), one may for a first approximation apply an elementary linear-additive equation. However, the necessary safety cannot be fully achieved by such a calculation alone. Fracture from incidental scratches exerted on the glass surface are more imminent and dangerous. The additivity principle from the chemical composition is only, perhaps, applicable as a rule of thumb when formally a mechanical strength better than 160 is guaranteed for the parameter F_m in the service of champagne bottles.

298. Furthermore, O. Knapp[94] contributed extensive experimental testing data (from more than 100 different silicate glasses) orienting differences of results of tests, combined with a calculation from the oxidic increments of composition which he assumed to have considerably improved to a reliable safety up to 98.1%, and with maximum deviations of about 1.03%. Corresponding calculations and tests were discussed for borosilicate glasses by the same author[95] for data of the thermal expansion coefficients. From a series of so-called "intermediate" and graded seal glasses (from American and British manufacturers) a calculation method was used in which the additivity first is restricted, for all the oxides as ingredients by their commonly used increments, with the exception of B_2O_3; the resulting numerical values are then deducted from the amounts of heat expansion, and the result is divided by the percentage in B_2O_3. This somewhat uncertain and rather tentative method gave on the graphic evaluation a certain conventional basis "constant" (0.8) for borosilicate transition (graded seal) glasses which contain from 0.7 to 31.6 wt % B_2O_3, but in every case are better and more useful for the technology of so-called "laminated glass" for high-vacuum instrumentation, than the usual chemical increment methods proposed so long ago (W. E. S. Turner and S. English, 1927), with an increment for B_2O_3 of 0.6 which should no longer be applied for glasses containing more than 12% B_2O_3. There is, in the opinion of Knapp, no boric acid anomaly for the thermal expansion coefficients.

299. H. A. Robinson[96] demonstrated in a meritorious investigation of the additivity principle for the calculation of physical properties parameters of simple binary alkali silicate glasses from additivity equations, that only the molar refractivity shows the desired accuracy in the data for this one optical property constant, with a linear correlation as the basis. For a relatively large number of other properties, however, Robinson found marked discontinuities and breakpoints in the diagrams as a func-

[94] *Sprechsaal* **101**, (4), 133–135 (1968).
[95] *Sprechsaal* **102**, (23), 1047–1048 (1969).
[96] *Amer. Ceram. Soc.* **52**, (7), 392–399 (1969).

tion of the ratios $R_2O:SiO_2$; $R_2O:O_2$; and SiO_2; R_2O (cf. Vol. VII. ¶ 663). We emphasize here only that the specific volume, the heat of formation, the logarithms of electric resistances, and the volatilization losses show such breakpoints; the two last-named parameters show even three and two linear ranges, respectively, for the validity of those functions. The working hypothesis was that structural reasons and changes in glass constitution must be the source of such phenomena, caused by interference with eutectic compositions superimposed on the normal glass response in the test of the properties named above. For the detection of the breakpoints, the best ratio, according to Robinson is that of $R_2O:SiO_2$, the use of which automatically assures that the property in question is studied on the basis of one mole of silica. The ratio for similar calculation most often applied in the previous literature was that of $R_2O:O_2$, i.e., on the basis of molecular oxygen in the glass composition. However, serious difficulties may arise, particularly when the behavior of small ions like Li^+ is to be studied. Robinson's thermodynamic opinion on the hiatus phenomena in internal heat contents or enthalpy changes are theoretically of highest significance for the role of the individual bonds of Si—O and B—O, to illustrate the absence of breaks in the relations with molar refractivity.

300. A highly interesting recapitulation of questions arising when the chemical increments for additivity calculations of physical properties are applied for glasses, i.e., the classical "factors" used by A. Winkelmann and O. Schott (1894), or those by F. Auerbach (1891 ff.), and newer ones by P. Beyersdorfer (1948), was recently presented by G. Weinmann[97] for a typical barium crystal glass, namely for its cubic expansion coefficient, the density, compressive and tensile strengths, scratch-hardness, and the refractive index. The lowest calculation class of errors was observed for the light refraction indices, with only 1 to 4%, whereas the tensile strength may show deviations from the average of 5 to 24%, the compressive strength may vary up to 25%, the hardness parameters even more. It may, in this connection be appropriate to recall that the enormous advancements in the technology of glass manufacturing made it possible to adapt borosilicate glasses to fulfill the most diversified requirements of all branches of industry for special glasses. We mention in this respect an excellent review of E. Preston[98] which contains a wealth of information from the newer literature.

301. Specifically, the *thermal conductance* of glasses in the temperature range from −150 and +100°C was extensively studied by E. H. Ratcliffe,[99] with many graphic diagrams and tabulated data for an examination of simply additive rules

[97] *Sprechsaal* **102**, (23), 1050 (1969).
[98] *Glass* **44**, (1), 12–18; (1967); **44**, (2), 60–68 (1967).
[99] *Glass Technol.* **4**, (4), 113–128 (1963).

and equations for a calculation of "most probable" values for this branch of glass technology. The data given for silica glass, Pyrex and Vycor (Corning) brands, and phosphate and borosilicate glass compositions are of the highest importance, not to speak of numerous economically well-introduced optical glasses, and the like. Attempts have also been made to develop additive equations which may give results for required accuracies and not above 5% in deviations, with reference to previous increment corrections as earlier recommended by O. Paalhorn (1894), F. M. Focke (1899), A. Russ (1928), D. E. Sharp *et al.*[100]

302. Thermodynamic properties of binary sodium silicate glasses from room temperature up to 800°C have been measured by K. Takahashi, T. Yoshio, Y. Miura, and T. Hirai,[101] with calculations of entropies and of heat capacity using experimental methods after W. Oelsen. The results are highly significant in evidencing how relatively little characteristics are influenced by changes in the chemical composition of the simplest alkali silicate glasses. This is explained by the relatively great similarity of all these glasses in their framework structures, after approximately one and the same stereochemical principles.

303. The problems of additivity for a series of physical properties as a function of the chemical composition have a particular meaning also for the boundary fields of thermodynamics, in the language of practical technological research; the determination of enthalpies and of the specific heat of glass, as demonstrated by recent investigations of Vr. Tydlität, A. Blažek, J. Endrias, and J. Staněk.[102] By 1894, A. Winkelmann[103] had already developed equations for interpolation, on the basis of assumptions concerning the additivity functional correlations existing for the specific heat, with changes in chemical composition for the short range from only 16° to 100°C. A step forward then was a calculation method found by A. Thuret,[104] which was applied by D. E. Sharp and L. B. Ginther,[105] for silica glass to build up an adequate additivity equation for $\bar{c}_p$, valid up to 1300°C and then used for a system more generally useful for the common technologically interesting complex glasses.[106] The mixing-calorimetric method (a copper block instrumentarium after the adiabatic principle) was furnished with advanced experimental tools, and with a higher degree of measurement accuracy continued by Tydlität *et al.* for $T = 600°$

[100] Cf. G. W. Morey, in his book "The Properties of Glass," 2nd ed., Van Nostrand-Reinhold Princeton, New Jersey, 1958.

[101] *Mem. Sch. Eng. Okayama Univ.* **2**, (1), 55–61 (1967).

[102] *Glastech. Ber.* **45**, (8), 352–389 (1972).

[103] *Ann. Phys. Chem. N.F.* **49**, 401–420 (1893).

[104] *J. Soc. Glass Technol.* **20**, 680–684 (1936).

[105] *J. Amer. Ceram. Soc.* **34**, (9), 260–271 (1951).

[106] See also D. E. Sharp and J. Moore, *J. Amer. Ceram. Soc.* **41**, (11), 461–463 (1958).

to 1300°C, and thermodynamically evaluated. In every case, the goal of satisfactorily accurate data for $\bar{c}_p$ was achieved in good agreement with those concluded from theory but we must not omit reference to the difficulties in using any mixing-calorimeter methods, namely, that the cooling conditions, particularly in the Cu block calorimeter, are not easily reproducible, and that a certain portion of the energy therefore is not determinable by an undercooling effect, the "residual" energy being a function of the rate of cooling.[107]

304. Interesting are measurements of adiabatic-elastic moduli for calcium aluminate glasses which were made by T. J. Sokolowski and M. H. Manghnani,[108] exposed at 25°C in a manganine cell under hydrostatic pressures from 1 to 3,500 bars (cf. Vol. VII. ¶ 401, 545), by a determination of changes in the speed of longitudinal and transversal waves, over an electronic oscillographic device based on ultrasonic interferometry.[109] The absolute values for the compression and shearing moduli and the Poisson ration were higher than is usual for silicate glasses.

305. Of great practical significance are measurements of *thermal shock resistance* of ceramic material of simple or multiphase composition, on which D. P. H. Hasselman[110] reported, and which inform us of the initiation and propagation of fractures and cracks in brittle materials. The theory of these processes is based on an energy balance after A. A. Griffith for a spherical sample, and is of fundamental importance for the design of brittle construction materials to be exposed to thermal shock effects.

306. W. Sack and H. Scheidler[111] discussed eminent problems of production and application of consumer glassware, on the basis of Na – Ca silicate, and Li aluminosilicate composition, with a raised temperature shock resistance. For such purposes, experiments make evident that the viscosity is the most important variable which determines all those phenomena and factors. Crystallization tendencies are of a secondary influence; during manufacturing, tendencies for unmixing (phase separation) are practically of no significance at all. It may happen only that an undesirable reduction in leaching (hydrolytic) resistance may be observed. This and other problems of prime importance for the production and treatment of lithium aluminosilicate glasses to be changed to Pyroceram (glass-ceramics) products must be care-

[107] On details of the construction and operation schedule for the copper block calorimeter after Vr. Tydlitát, A. Blažek, and J. Haloušek, see *Czech. J. Phys. B* **21**, 817–822 (1971).

[108] *J. Amer. Ceram. Soc.* **52**, (10), 539–542 (1969).

[109] Cf. E. Schreiber and O. L. Anderson, *J. Amer. Ceram. Soc.* **49**, (4), 184–190 (1966).

[110] *J. Amer. Ceram. Soc.* **52**, (11), 600–604 (1969); cf. A. A. Griffith, Phil. Trans. Roy. Soc. (London) **221A**, (4), 163–198 (1920); Proc. Int. Congr. Appl. Mech; 1st, Delft, 1924, pp. 53–63.

[111] *Glastech. Ber.* **43**, (8), 322–326 (1970); **43**, (9), 359–368 (1970).

fully examined and surveyed over the viscosity ranges between 10^4 and 10^{14} P. The range from 10^5 to 10^8 is, on the other hand, the interval in which devitrification tendencies are released (cf. Vol. III.A. ¶ 39 ff.).

MECHANICAL PROPERTIES AND CHEMICAL COMPOSITION OF GLASSES

307. Another field of great significance in its dependence on important physical properties of commercial glasses on their chemical composition encompasses the mechanical properties, notably the fatigue phenomena and mechanical strengths. This was investigated by M. Watanabe, R. V. Caporali, and R. E. Mould,[112] for common Na – Ca silicate glasses, in the pristine state and after an abrasion of the surface layers by grit blasting or jet-blasting with silicon carbide powder ("standardizing"), combined with variant treatments at the temperature of liquid nitrogen, and different aging exposures in water steam, or in liquid nitrogen and water, one after the other. In every case, the aging effects increase the tensile strengths of the samples considerably; for different glass compositions, increases of more than 100% can be measured, whereas a fatigue test merely discloses a reduction in mechanical strengths by about 50%, in comparison with aged samples. The higher the Na_2O content of the glass, the higher the increase in strength by grit blasting. The authors discuss these observations chiefly as an effect of water on the surface films, whereas the influence of the chemical composition indicated in the fatigue phenomena is a direct reaction of water molecules on the glass structures by mechanical strain.

308. All these effects are also marked for other properties of glasses, e.g., deviations from direct-linear ("ideal") functional correlations to the molecular volume parameters.[113] A nonlinear correlation to the cation-exchange conditions is seen, e.g., from the appearance of a maximum in electrical conductance. Watanabe, Caporali, and Mould[114] extended their observations also to mixed glasses of the system $K_2O - Li_2O - Al_2O_3 - SiO_2$, in the pristine (nonabraded grit-blasted) states of specimens in their very characteristic changes of mechanical strength under thermal aftertreatments, but before nucleation and crystallization form typical glass-ceramics, in different states of fatigue reactions (cf. Vol. III.A. ¶ 39 ff.). Nevertheless, the earlier (1961) experiments of those authors made impressive how variable the dependence of strength properties are on the chemical composition of glasses from one condition of pretreatment and testing method to another, evidently by

[112] *Phys. Chem. Glasses* **2**, (1), 12–23 (1961).

[113] Cf. Caporali, *J. Amer. Ceram. Soc.* **47**, (8), 412–413 (1964).

[114] Symp. Nucleation Crystall Glasses Melts, Monograph, Amer. Ceram. Soc. 1962, pp. 21–28.

highly complicated interactions between composition effects *per se* on the mechanical properties, and the aging response after fresh abrasion treatment, and the permanent effects of static fatigue, these effects counteracting each other in an intricate manner.

309. From the industrially interesting problems of grit blasting effects on the surface of glass, and the mechanical behavior of it as a function of composition, it is only one step to the question of how *wear resistivity* is to be interpreted in this respect. This problem is identical with that of the behavior of common ceramic *glazes* (of variant composition and nature of the turbidity agent), under the influence of wear treatments, as investigated by H. W. Hennicke, H. E. Schwiete, and J. Sieckmann.[115] The testing methods chosen by these authors cover simple measurements as found in the literature, e.g., that of increasing thinness of layers and corresponding weight losses, those of "gloss" specifically for glaze tests, and of rugosity in the surfaces, as determined with a *profilometer*, which can detect even the early effects of abrasion damage. Under the indentation tests, the elastic recovery of a glaze surface showed a larger effect than the true abrasion resistance which is generally, in technology, called the "hardness."

310. Starting from the classical methods for *microhardness*, namely in the first line, the Vickers diamond pointer indentation method, a systematic examination of the behavior of glasses,—from the softest one (that of selenium) to the hardest one (silica)—was achieved by M. Prod'homme,[116] who is of the opinion that there is a tolerably good agreement among the rich data in literature. An important observation is that pretreatments by fire or mechanical polishing have no substantial influence on the numerical results of the Vickers indentation test. It is also important to know that over a period of several months of systematic periodical distances, no irregularities were observed in reproducibility. (On correlations of the microhardness to viscosity, see Vol. VII. ¶ 124).

311. Taking the *microhardness* of special glasses as an example, low-in-alkali glasses are generally adopted for glass-fiber manufacturing; most of the commercial brands of this class contain boric acid as an essential oxide ingredient. For economical reasons, in the USSR new glasses belonging to the system $CaO-MgO-SrO-Al_2O_3-TiO_2-SiO_2$ have been developed which are claimed to be even superior in quality to those commonly used types for glass-fiber manufacture, namely of aluminoborosilicate composition. M. A. Matveev and V. M. Solodukho[117]

[115] Tonind. Z. **90**, 106–117 (1966); **90**, (4), 147–155 (1966), with a very valuable literature bibliography, and a detailed discussion of the theoretical background of different abrasion test methods.

[116] *Phys. Chem. Glasses* **9**, (3), 101–105 (1968).

[117] *Silikattechnik* **19**, (6), 181–183 (1968).

studied several sections of the polynary-TiO_2-containing glasses and tested their tensile strengths. For a constant content of silica, lime, and alumina, the microhardness data increase symbatically with an increasing content of titania, whereas, a variation of CaO in the limits from 5 to 20 mole% proved to have no major effects.

312. A systematic study of correlations among wear and abrasion tests, microhardness, and high-rate of fracture propagation test method, was made to *optical* glasses of widely variant chemical composition by Fr. Kerkhof and M. Schinker[118] (Fig. 86). From the practical viewpoint there were particularly significant tests of abrasion in different liquid media, water, pure *m*-xylene, in which 0.1 mole stearic acid was dissolved[119] which evidently show considerable influence on the amounts of gravimetric material abrasion. Highest wear was observed in the stearic acid containing xylene solution, a moderate value in distilled water, the lowest one in pure xylene.

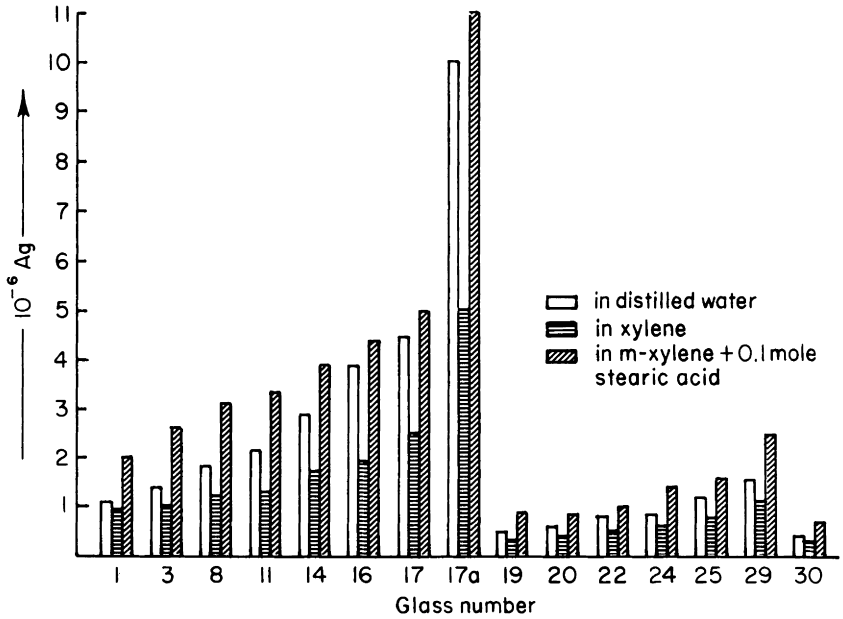


FIG. 86. Weight losses by abrasion (A_G) of fifteen different optical glasses as measured for three different grinding liquids. (Kerkhof and Schinker.)

[118] *Glastech. Ber.* **45**, (6), 228–233 (1972).

[119] Cf. the previous investigations on the same problem by W. von Engelhardt (1942) for quartz, and by R. Ramsauer, *Glastech. Ber.* **21**, (10), 239–247 (1951); cf. Vol. I.C. ¶ 334.

For brittle manufacturing conditions, there are definite correlations between the gravimetric abrasion amounts and those of the Vickers and Knoop indentation tests of microhardness, further with the maximum speed in fracture propagation.

313. It is possible to calculate the *surface tension* of a given glass melt at temperatures up to 1200°C with an indirect practical method through determination of the surface hardness (chiefly the Knoop indentation hardness tester of the given glasses, as previously was done by A. E. Pavlish and I. Mockrin.[120] C. Rubenstein[121] based his calculations of the surface-tension parameters from the additive increments for the oxidic constituents of given glasses (see the older data determined by K. C. Lyon).[122] Rubenstein subjected the available numerical data of the oxide increments to a critical reexamination, with the important practical result that reasonably accurate data are those found in literature for SiO_2, Al_2O_3, B_2O_3, CaO, MgO, Na_2O, K_2O, BeO, SrO, BaO, ZnO, CoO, GeO_2, PbO, ZrO_2, CeO_2. Those for other oxides should be used with critical care; the least reliable ones being those for P_2O_5, V_2O_5, and Li_2O; and those for Fe_2O_3, TiO_2, CuO, CdO, NiO, Sb_2O_3, and SnO_2 being of tolerable accuracy for estimations of surface tensions.

314. Among the glass properties which are sensitive to structural and specifically electronic configuration responses in glass constitution, we refer briefly by discussions of such relationships in T. Moriya's microphase or "micellar" theory[123] which are repeatedly outlined in our text. For more practical technological aspects, we equally cite the excellent investigations by V. Gottardi, B. Locardi, A. Bianchini, and P. L. Martini[124] who studied the occurrence of structural compactions in the system $K_2O-PbO-SiO_2$, which characteristically coincide with maxima in microhardness, and minima of volatilization for PbO and reduction of PbO to Pb, at three different temperatures. The system $Na_2O-PbO-SiO_2$ and its glass phases show such phenomena, with higher ratios Si:O than those observed in the potassium containing one. We showed in ¶ 239 that it is quite evident here that effects of the same characteristics occur, only modified by the higher polarization power of the Na^+ ions in comparison with K^+ (cf. ¶ 239). In another direction, C. Bettinali, V. Gottardi, and B. Locardi[125] (cf. ¶ 155) could demonstrate that photoluminescence in the system $K_2O-PbO-SiO_2$ shoes a singular phenomenon for a glass with 20 wt. % PbO, i.e., for a quite distinct singular ratio Si:O in the glass structure. A hypothesis that neighboring Pb atoms in the structure interact with emitting

[120] *J. Amer. Ceram. Soc.* **30**, (2), 54–63 (1947).
[121] *Glass Technol.* **5**, (1), 36–40 (1964).
[122] *J. Amer. Ceram. Soc.* **27**, (6), 186–188 (1944).
[123] *Bull. Tokyo Inst. Technol.*, No. 66, 29–79 (1965).
[124] *Glass Technol.* **9**, (5), 139–144 (1968).
[125] *J. Noncryst. Solids*, No (1), 360–370 (1969).

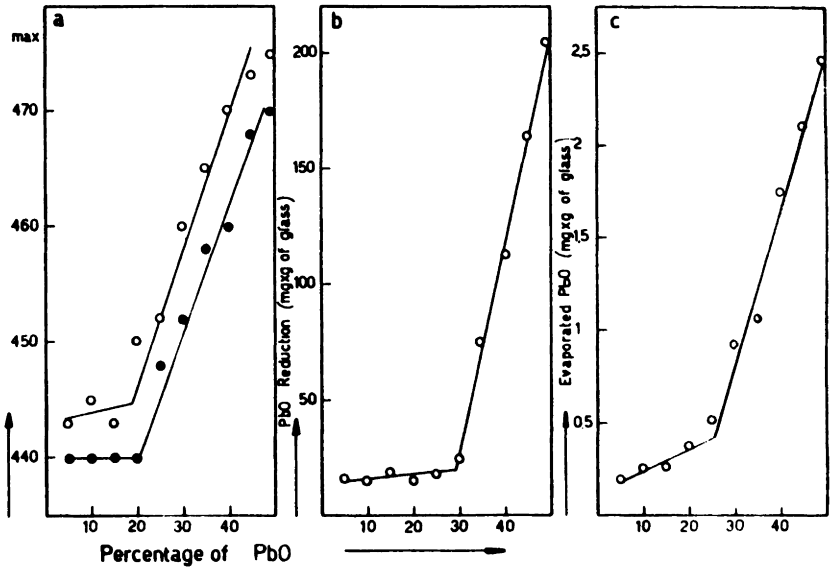


FIG. 87. Relationship between the content of PbO (in wt. %) and properties of different glasses as wavelength values related to emission maxima at 120°K and 300°K, PbO reduction and evaporated PbO. (Bettinali, Gottardi, and Locardi.)

Pb atoms when the concentration in Pb is increasing could, in this case, be made evident by a shift observed in the emission maximum towards the red, for glasses with 20 to 25 wt % PbO, the corresponding temperatures being 120° and 300°K (cf. Fig. 87).

315. The *electrical* properties of alkali-free borate glasses were examined by E. Gough, J. O. Isard, and J. A. Topping[126] for the systems $RO-Al_2O_3-B_2O_3$ and $PbO-Bi_2O_3-B_2O_3$, between 100 Hz and 40 GHz, as a function of temperature (cf. Vol. VII. ¶ 205, 243). The activation energy for direct current conduction depends solely on the molecular composition, and is independent of the variation of the R^{2+} cations (of Ca, Ba, Sr). It depends only on the anionic structure, i.e., an O^{2-} anionic migration, whereas, for R = Pb, the activation energy is reduced. For the system $Bi_2O_3-B_2O_3$, it is assumed that the conductivity is electronic and not ionic. The dielectric constants increase in a nearly linear functional relation with the concentration of the cations, at normal temperatures; at elevated temperatures, however, losses occur which must cause a dispersion of the dielectric constants and losses in direct current conductivity which are similar to migration losses, as known

[126] *Phys. Chem. Glasses*, **10**, (3), 89–100 (1969).

from alkali silicate glasses. All three glasses show a typical residual loss which slowly increases symbatically with the frequency, but is independent of the temperatures. From the width of the frequency range, it is concluded that there is resonance with cation vibrations, but assumed to be electron jump reactions. Residual hydroxyl anions may, last not least, play some subordinate, but not negligible role, in all these phenomena.

316. Those interesting bismuth–lead borate glasses, as mentioned before, are also known from earlier studies by P. F. van Velden,[127] from the systems $PbO-Bi_2O_3-SiO_2$; $PbO-Bi_2O_3-Al_2O_3-SiO_2$; $BaO-Bi_2O_3-SiO_2$; and $BaO-PbO-SiO_2$, all with low concentrations in alumina in silica. In the present case specific emphasis is given to heat conductivity properties, and a determination of increments (factors) for the constant temperature of 40°C, in a calculation based on the additivity principle. The increments for alumina and silica increase when the ratios $O:SiO_2$ and $O:(SiO_2 + Al_2O_3)$ are above 3. Therefore, for a selection of glasses with a possibly low heat conductance, the alumina and silica contents must be kept low, i.e., the ratios mentioned are above 4. Particularly interesting is a clear transition from the "conventional" type to the "invert" type, following the interpretation by H. J. L. Trap and J. M. Stevels,[128] i.e., of intrinsic constitution reactions in the lead–bismuth glasses from the structural type with pronouncedly different short-range phenomena, as manifested here by substantial decreases in the silica factor when the transition into the invert type takes place. On the other hand, alumina shows just the contrary behavior.[129] Higher temperatures apparently promote the decrease in the SiO_2 factor, and the increase in the alumina increment as the glass structure shifts toward the invert type. In every case, the lead–bismuth glasses systems are of a very high practical interest in respect to uses for glasses as a coating of low heat conduction and heat insulation.[130]

317. According to A. N. Tiwari and C. E. Subbarao[131] in the system $Bi_2O_3-P_2O_5$ glass formation takes place up to 63.8 wt. % (35 mole %) Bi_2O_3. Highly remarkable are maxima of the activation energy of conduction, microhardness, and minima for thermal expansion at about 20 mole % Bi_2O_3 which coincide with an abrupt increase in the deformation temperature at the same composition. The explanation of this remarkable fact may be found in terms of a change in the structural function of Bi^{3+} ions from a framework-forming, to a framework-modifying type, in agree-

[127] *Glass Technol.* **6**, (5), 166–169 (1965).
[128] *Glastech. Ber.* **32.K**, VI. 31–VI. 52 (1959).
[129] Cf. E. D. Lacy, *Phys. Chem. Glasses* **4**, (6), 234–238 (1963).
[130] Cf. H. Ratcliffe, *Phys. Chem. Glasses* **1**, (3), 107–118 (1960); **4**, (4), 193–205 (1963).
[131] *J. Amer. Ceram. Soc.* **53**, (5), 258–261 (1970).

ment with J. M. Stevels' theoretical deductions on the characteristic values R for the average number of oxygen atoms per framework-forming ions X, the average number of nonbridging O^{2-} anions Y, and the number of bridging oxygen atoms per polyhedron Z in this extremely interesting glass; the highly polarizable ions Bi^{3+} and Pb^{2+}, therefore cause a very high refractive index, and dielectric constant.

TITANIA-MODIFIED GLASSES AND THEIR PHYSICAL PROPERTIES

318. We start this industrially highly important chapter concerning the conditions of physical properties with a series of publications made by Bh. V. Janakirama Rao, first on the influence of those of the system $K_2O-PbO-SiO_2-TiO_2$, and its relations to structural problems.[132] The basic glass contained 25 wt. % K_2O constantly, while the other glasses contained a PbO content from 0 to 60 wt %, silica systematically being replaced by titania. Increasing the TiO_2 content raised density, refractive index, the thermal expansion coefficient, and the dielectric constant, although the functional relation of chemical composition and titania concentration rather often was subjected to deviations from a simple additivity rule. For the Littleton point temperature, the additivity increase is observed but reaches a certain maximum, and then decreases with an increasing titania content. In parallel with this behavior, the thermal expansion coefficient first decreases with increasing TiO_2 contents, then reaches a minimum, after which it shows a tendency to increase (cf. Figs. 88 and 89). The position of those maxima and minima depends entirely on the contents of PbO in the basic alkali silicotitanate glass composition. There is a substantial increase in chemical durability, even under the action of small additions, but this effect is of less importance for higher TiO_2 concentrations.

319. Rao interprets this phenomenon by the assumption that the rapid increase in the improvement effect corresponds to the formation of the coordination group $[TiO_4]$ when the appearance of $[TiO_6]$ occurs at higher contents of TiO_2. These changes indicate first a reduction of the strength of the framework in the glass constitution, later a distinct weakening and consolidation. The Ti^{4+} cation therefore, plays a double role in the system $K_2O-PbO-SiO_2-TiO_2$ insofar as opposite effects occur in the oxygen packing and in the properties like the viscosity and expansivity. Ti^{4+} ions decrease the ionic characteristics in the system, whereas Pb^{2+} promotes it. Janakirama Rao[133] underlines this dual behavior of Ti^{4+} also in the ternary partial system $K_2O-SiO_2-TiO_2$, with entirely opposite actions in different

[132] *J. Amer. Ceram. Soc.* **46**, (3), 107–114 (1963).
[133] *Phys. Chem. Glasses* **4**, (1), 22–34 (1963).

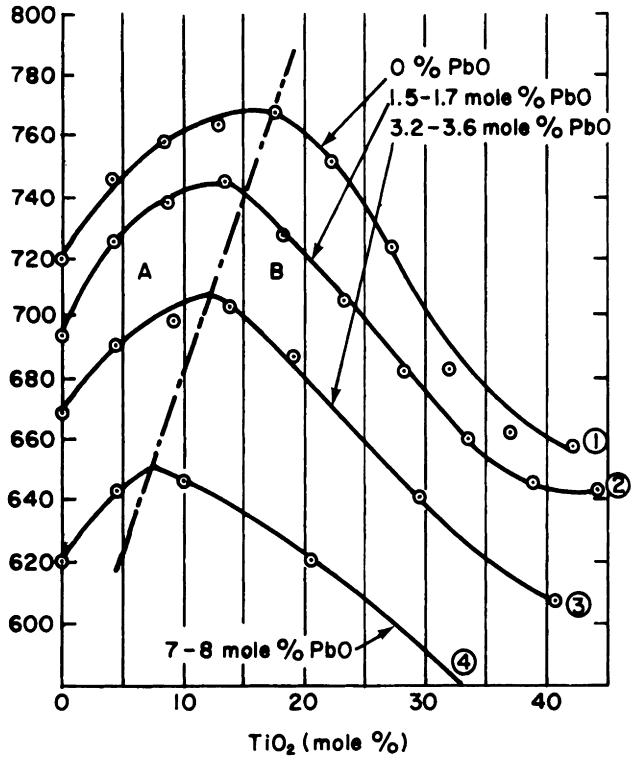


FIG. 88. Influence of titania on the softening temperatures of glasses of system $K_2O-PbO-SiO_2-TiO_2$. Compositions on the left-hand side of the points of inflection of the curves constitute region *A*; those on the right-hand side constitute region *B*. (Janakirama Rao.)

directions, not only in the refractive index, but also in the thermal expansion coefficients and in tensile strength and other parameters. Ti^{4+} is a typical framework-former cation in its "own right," depending on the coordination change reactions $[TiO_4] = [TiO_6]$ on quite specific conditions, strengthening the glass structure when is in tetrahedral coordination, weakening it in the octahedral coordination with O^{2-} anions. These properties tend to establish equilibrium in the form of $[TiO_4]$ for the high-in-silica concentration regions, and in favor of $[TiO_6]$ in the lower siliceous area of the ternary system. Rao[134] extended his studies to binary alkali titanate glasses which are only available by extremely rapid quenchings of small charges corresponding to 28 to 60 mole % K_2O and Rb_2O; 25 to 67 mole % Cs_2O concentrations. The density, refractive indices, viscosity data, thermal expansion coefficients,

[134] *J. Amer. Ceram. Soc.* **47**, (9), 455–463 (1964).

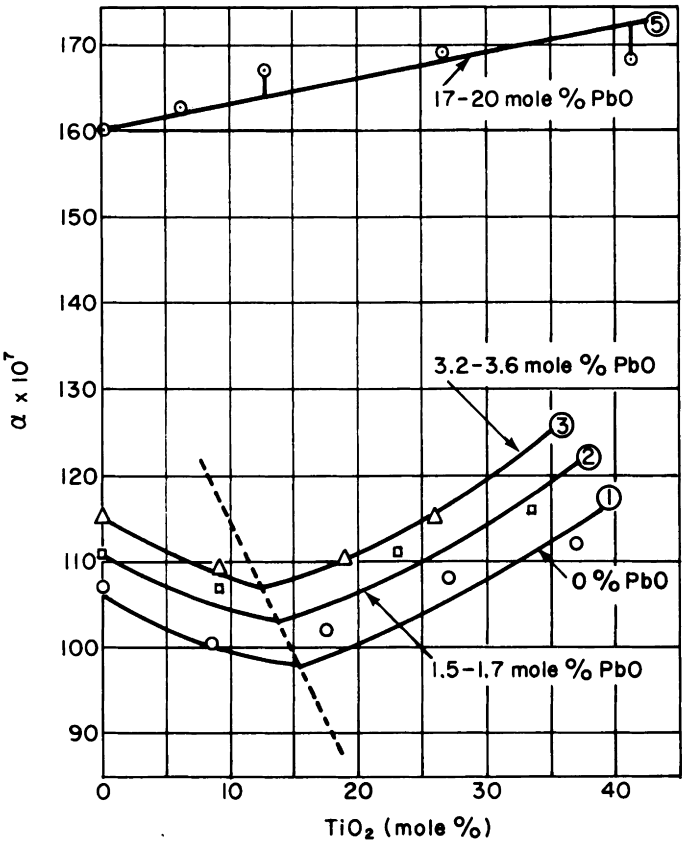


FIG. 89. Influence of titania on the coefficients of thermal expansion of glasses of the system $K_2O-PbO-SiO_2-TiO_2$. (Janakirama Rao.)

and the infrared emissivity were measured, including valuable observations on tendencies for nucleation and crystallization of TiO_2, and the hygroscopicity of the products. The glasses are anomalous for the viscosity and nucleation properties insofar as glasses with distinctly *higher* viscosity devitrify *more easily* than the more fluid glasses. The alkali oxide vibrations in the infrared spectra over the range from 1- to 16-μ wavelengths are nearly completely identical over the liquid–glassy and the crystalline–solid phases.

320. The $[TiO_6]$ coordination of the Ti^{4+} ion is, in every respect, a true glass-forming central atom in the glass structure, a fact which makes urgent a certain generalization of the chemical formulation which W. Zachariasen (1932) gave for the glass-building atom rules, and which, in their original formulation, restricted glass formation exclusively to the condition of a tetrahedral coordination of the central

cation in the glass structure. Therefore it limited the "permissible" or better "critical" ratio of the cation radius in bonding with O^{2-} to 0.414, whereas, the ratio for $Ti^{4+}:O^{2-}$ radii is, in this case, higher than the theoretical limit is fixed. The surprising fact must be noted that in alkali titanates the existence of true *ortho*-titanate glasses, R_4TiO_4, is established (cf. Vol. VII. ¶ 408).

The infrared spectra of the titanate glasses with a higher content of TiO_2, do not show any changes from the $[TiO_6]$ into $[TiO_4]$ vibration bands, i.e., the fact exists that Ti^{4+} in glassy phases of alkali titanates is in the sixfold coordination.

321. Another publication by Janakirama Rao[135] which we have to rediscuss more extensively in connection with the problems of glass-ceramics (cf. Vol. III.A. ¶ 37 ff.) emphasizes the strong tendencies for nucleation and crystallization from alkali titanate glasses which they have in common with those in corresponding silicotitanates, -niobates, -tantalates, and the systems $R_2O-GeO_2-Ta_2O_5$, all with very individually interesting physical and, particularly, electric properties. The facts observed with "nucleation agents" are reconfirmed in this new class of chemical compounds. One is tempted to see a higher probability for the postulates of the classical crystallite hypothesis of glass constitution and also to the assumption of "micellar systems" with precrystallization phenomena, and somewhat extreme details in the behavior of such glasses, as described by Rao. He feels justified in recommending intensified investigations into the general field of nucleation and crystallization of glasses of all kinds, and in distinction from "neoceramics" in their properties.

322. Rao also defends his wide-branching opinions against critical remarks made by W. B. White[136] who attributed anomalies to a cooperation with carbonate anions, and to the presence of water (hydroxyl groups) in binary alkali titanate glasses, for developing the $[TiO_6]$ coordination. On the contrary, Janakirama Rao[137] could give full evidence of his conclusions in regard to the $[TiO_6]$-type groups in titanate glasses, by infrared absorption spectra of $Rb_2Ti_2O_5$ glass molten from Rb_2CO_3, $RbNO_3$, and RbOH, in comparison with spectra of $BaTiO_3$, and of monocrystals of TiO_2 (rutile). All the spectra of these products give evidence that R_2O–TiO_2 glasses exist without any water content or residual CO_3^{2-} anions which should be indicated by infrared absorption bands, or any contamination indicated by a band near 3300 cm^{-1}, but very distinctly show the 495- to 610-cm^{-1} vibration bands of the $[TiO_6]$ groups alone (cf. Fig. 90).

323. Some "Cabal"-type *aluminate* glasses also containing titania are highly

[135] *Glass Technol.* **5**, (2), 67–77 (1964).
[136] *J. Amer. Ceram. Soc.* **48**, (2), 108–109 (1965).
[137] *J. Amer. Ceram. Soc.* **48**, (11), 602–603 (1965).

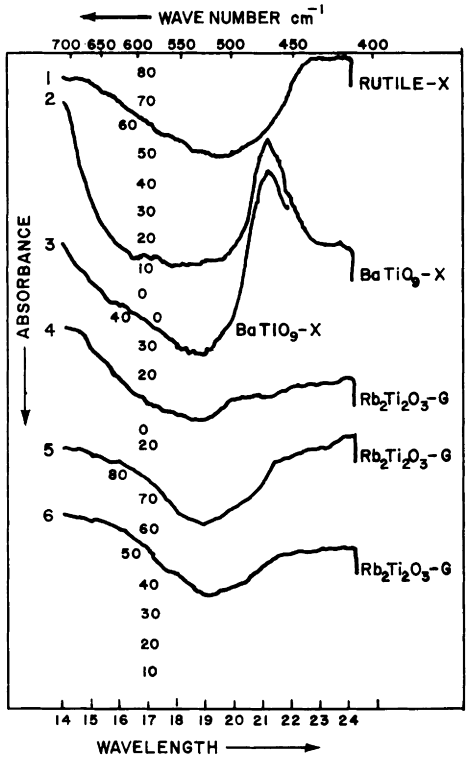


FIG. 90. Infrared spectra of transparent glasses of $Rb_2Ti_2O_5$ composition, of $BaTiO_3$, and rutile for comparison as crystalline phases. (Janakirama Rao.)

interesting in respect to their dielectric properties, chiefly low loss factors (tan δ), and in increased dielectric constants, without any essential change in their temperature coefficients, as was demonstrated by M. Monneraye, J. Serindat, and C. Jouwersma,[138] even when CaO is replaced by SrO or BaO in the composition type $RO-Al_2O_3-B_2O_3$. When nucleation and crystallization are indicated in the manner that glass-ceramics are produced with TiO_2 as the nucleator agent (cf. Vol. III.A. ¶ 37 ff.) the resulting products have dielectric constants increased to 6.15–11.41. The crystallization of rutile and anatase (cf. Fig. 91) is confirmed in these. It is practically remarkable that glasses on the basis of the system $SrO-Al_2O_3-B_2O_3$ of the family discussed have much desirable dielectric properties, namely a low power factor and a sufficient amount of crystallized rutile (cf. ¶ 350). A certain compromise must be admitted since, with the increasing content of B_2O_3 in such glasses the crystallization tendency and the power factor are reduced.

[138] *Glass Technol.* **6**, (4), 132–137 (1965).

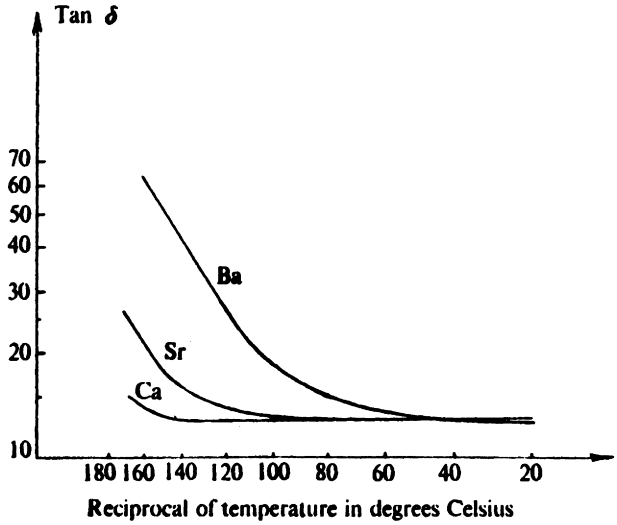


FIG. 91. Power factor as a function of log reciprocal temperature for different TiO_2 containing alkaline earth Cabal glasses. (Monneraye, Serindat, and Jouwersma.)

324. S. V. Bhatye[139] studied effects of small additions of (3%) TiO_2 to Na–Ca silicate glasses containing also small amounts of B_2O_3. When the addition of the last-named oxide chiefly reduces the melting and fining time periods (therefore, also the working range), Al_2O_3 acts in the opposite direction, raising the low-temperature viscosity. TiO_2 resembles B_2O_3 in its affects on the high-temperature viscosity characteristics; B_2O_3 improves the chemical durability even more than alumina and titania, as is demonstrated by an extensive tabulation of the single parameters (no electric properties were measured). For the viscosity, A. vanBemst and C. Delaunois[140] measured the influence of TiO_2 on the viscosity properties in the ternary system $K_2O-SiO_2-TiO_2$, which are of great industrial importance for the constitution of the so-called "rutile slag" used in electric arc welding containing about 50% TiO_2.

325. From the metallurgical literature, it is known that basicity–acidity conditions play an essential role in the physical-chemical behavior of $CaO-Al_2O_3-$ titanate slags.[141] The amphoteric role of titanium in the system $K_2O-SiO_2-TiO_2$ is, according to V. Jankirama Rao (cf. ¶ 319 ff.), of particular importance for these

[139] *Bull. Centr. Glass Ceram. Res. Inst.* (*India*) **12**, (4), 111–116 (1965).

[140] *Verres Refract.* **20**, (6), 435–447 (1966).

[141] Cf. M. G. Frohberg *et al.*, *Arch. EisenHüttenw*, **33**, 421 ff. (1962); **36**, 477 ff. (1962); cf. II.C. 63 ff.

conditions; vanBemst's and Delaunois' measurements with the hot-stage microscope extended particularly to a study of the primary crystallization of rutile. The rapid decrease in viscosity from the increasing substitution of silica by TiO_2, is most striking for 10 to 23% TiO_2; above 40% TiO_2, however, the viscosity again decreases, the effects of TiO_2 are reversed, and crystallization is abundant, as in neoceramics, according to Rao. In the logarithmic viscosity versus % K_2O/SiO_2 diagrams, one may distinctly distinguish a "normal," i.e., linear-functional behavior range, and a sudden change of the activation energy of flow from 20 to 35 kcal/mole as soon as 12.5% TiO_2 is introduced into high acidity melts.

326. In the system $MgO-Al_2O_3-SiO_2-TiO_2$, S. Kumar and B. B. Nag[142] crystallized glass compositions like 15.5 wt. % MgO; 19.5 wt. % Al_2O_3; 58.5 wt. % SiO_2; 6.5 wt. % TiO_2, at 900° to 1140°C to determine the activation energy of direct, and alternate current conduction, before and after crystallization (in the first case 32.0 and 27.4 kcal/mole, in the second case 18.5 and 11.6 kcal/mole). The crystalline phase in the devitrified samples could be identified by X-ray diffraction methods as a blue-stained magnesium–aluminum titanate in which a certain amount of Ti was present in the form of the Ti^{3+} cation. The samples are pronounced semiconductors, showing sharp changes in electric properties with an apparent dielectric relaxation peak on the curves. With increasing crystallization temperatures, the electric properties, the crystallochemical nature of these phases, the size of the crystallites, and their morphological character change systematically. It is assumed that the crystalline phases of nonstoichiometric composition are typical semiconductors. A dielectric relaxation band was observed in the high-frequency range, probably due to Maxwell–Wagner losses of the heterogeneous dielectric containing semiconducting crystals. The activation energy for alternate current conductance (11.6 kcal/mole) after crystallization (see above) was significantly lower than the corresponding direct current value (18.8 kcal/mole), and is associated with an electron transition from defect sites in the nonstoichiometric titanates (cf. Figs. 92 and 93).

327. In the polynary system $CaO-MgO-SrO-Al_2O_3-SiO_2-TiO_2$, M. A. Matveev and V. M. Solodukho[143] (cf. ¶ 311) showed that the addition of TiO_2 as a simple "fluxing agent" for glass in automatic-continuous fiber-spinning processes is of great industrial importance, as are a certain increase of microhardness and distinct improvement of mechanical strength characteristics brought about by the introduction of TiO_2.

328. A counterpart of the studies of $BaO-B_2O_3-SiO_2-TiO_2$ ($+Ti_2O_3$) glasses

[142] *J. Amer. Ceram. Soc.* **49**, (1), 10–14 (1966).
[143] *Silikattechnik.* **19**, (6), 181–183 (1968).

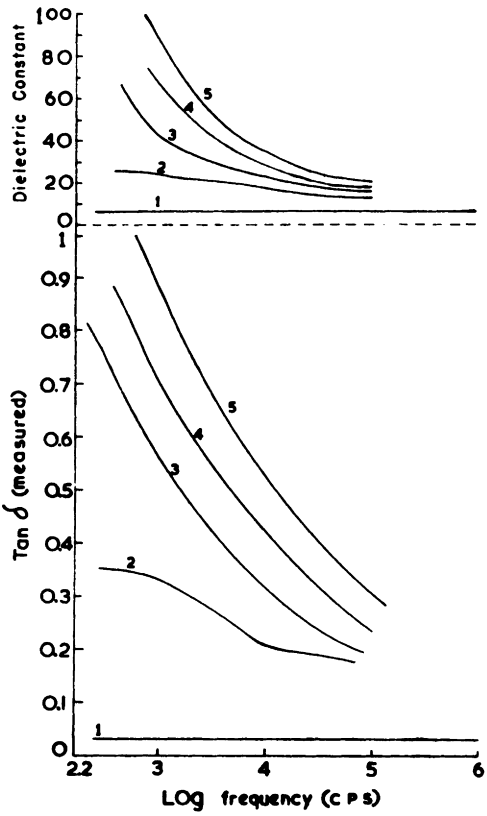


FIG. 92. Dielectric constant and power factor vs. log frequency for an uncrystallized glass of the system $MgO-Al_2O_3-SiO_2-TiO_2$, at (1) 24°; (2) 441°; (3) 500°; (4) 550°; (5) 600°C. (Kumar and Nag.)

previously made by M. Monneraye *et al.* (cf. ¶ 323), was performed by T. Takamori, H. Seo, and M. Tashiro[144] who studied the direct current electric conductance up to 500°C. The interreaction between the ions Ti^{4+} and Ti^{3+} is easily observed by the spectroscopic method at room temperature. It is of practical importance to note how much the initial composition of the glass batches, chosen for their production may influence the electrical resistivity of the resulting glass in a pure argon atmosphere. It is clearly evident that glasses containing *either* Ti^{4+} only, or Ti^{3+} only, as such, have a rather low conductance; but, in contrast, in another experimental series, when the base glass of the equimolecular composition BaO, B_2O_3, SiO_2 was *first* molten, *then mixed* with two other glass melts, one containing only

[144] *J. Amer. Ceram. Soc.* **52**, (11), 582–585 (1969).

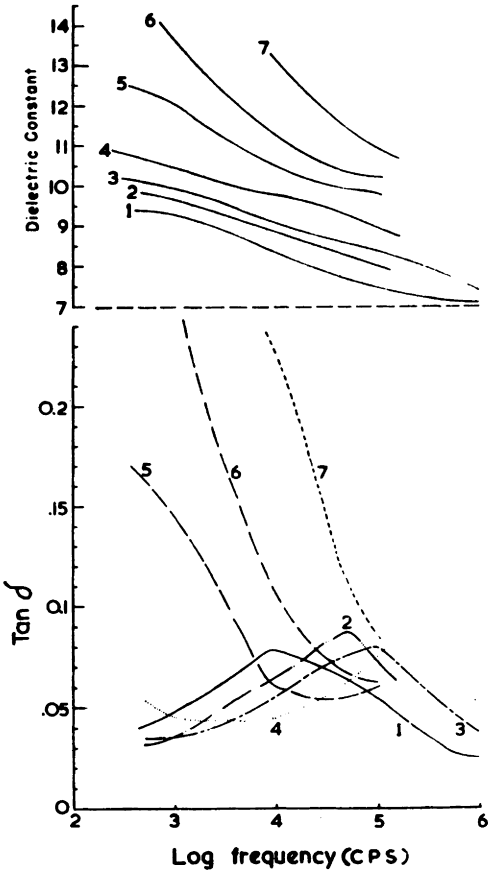


FIG. 93. The same functions for the crystallization product of the same glass after treatment at 1000°C. The data refer to experimental temperatures of (1) 23°; (2) 46°; (3) 62°; (4) 102°; (5) 163°; (6) 200°; (7) 250°C. (Kumar and Nag.)

Ti^{4+}, the other only Ti^{3+}, the end result was a glass which had a considerably higher conductance.

OPTICAL PROPERTIES OF GLASSES

329. We absolutely do not want to omit a brief reference to recent literature concerning the specific interest the optical industries take in the usefulness of new types of glasses of much variant composition classes marked, e.g., by the presence of rare-earth elements in their constitution and composition, in spite of the fact

that we discussed these in previous Chapters of our Report, and which we now take the opportunity to remind our readers of a few selected publications; we refer to these (cf. ¶ 147 f., 156).

G. F. Brewster, J. R. Hensler, J. L. Rood, and R. A. Weidel[145] circumscribe observations and correlations of the optical properties, chiefly the partial dispersion characteristics of some newer types of borate and phosphate glasses to emphasize their distinguishing marks by analytical constants and the properties of silicate glasses with valuable critical remarks concerning the higher requirements postulated for the accuracy in the determination of refractive index, dispersion, and corrections to be applied.

330. F. C. Lin, R. D. Haun, and R. C. Ohlmann[146] described some emission and absorption particularities of glasses containing rare-earth elements in their spectroscopic characteristics, like the trivalent cations of Nd, Pr, La, Er, Eu (also divalent), Ho, Dy, and others, in glasses of best qualities, recalling the previous suggestions given by E. Snitzer for maser glass[147] specifically also for the new fields of *lasers*.

331. Specifically, for lanthanum-containing high-quality glasses, see S. K. Duprovo and A. D. Shnypikov,[148] who studied the influence of an increasing content of La_2O_3 on changes in fundamental physical properties, to which we may add an extensive review of rare-earth glasses[149] for wide fields of applications, not only for laser purposes, but also for the manufacture of color television devices—or for cerium compounds, their absorption behavior in the ultraviolet range below 3,900 Å and particularly useful and efficient when combined action of Ce and Ti in special glasses.

332. J. Fanderlik[150] presented an explicit report on new developments in lanthanum glasses of high refractive index, and low dispersion and of fluoride- and fluorophosphate glasses (cf. Vol. II.B. ¶ 139), with low and high Abbe coefficients for special optical purposes, in details of the chemical composition and manufacture particularities, with numerical data on the spectral transmissivity, chemical durability, the volatilization losses during the fusion period in manufacturing, and their workability. The future evolution of such lanthanum (more generally, rare earth) special glasses

[145] *Appl. Opt.* **5**, (12), 1891–1894 (1966).

[146] *Advan. Glass Technol.*, Pt.II. 53 f. (1963).

[147] *Phys. Rev. Letters* **7**, 444–446 (1961).

[148] *Izv. Akad. Nauk S.S.S.R. Ser. Neorgan. Mater.* **2**, (9), 417–421 (1966) (Engl. transl.); (cf. II.A. ¶ 388).

[149] Edited by the Thorium Ltd., Major Extension in Glass **45**, (12), 471–473 (1968).

[150] *Veda a vyskum prum. sklarskem* **10**, 17–65 (1967).

with quite specialized characteristics are found in systems derived from the ternary type $B_2O_3-La_2O_3-ThO_2$, to which the oxides Ta_2O_5, Nb_2O_5, ZrO_2, and CdO, were introduced, as enumerated in the reports of the State Glass Research Institute of the ČSR.

333. H. Shröder,[151] reports a series of most recent advances in the technology efficiency of optical glass for all kinds of photography, reproduction techniques, photometry, holography, telescopy, and microscopy; the development of ultralens speed camera objectives and other special devices the evolution of superachromate objectives with negligible color aberration, increased infrared transmission for image transmitters, temperature-independent optical instruments of most versified classes, fiber-optical (light guider) systems, and the like. This review presents a most fascinating survey of the past 20 years.

334. Very recently, H. H. Käs[152] theoretically and experimentally discussed the fascinating problem of how, for the dispersion of certain glasses, it may be possible to modify the optical effects by the insertion of additional absorption bands, when concentration, electron damping, and resonance effects of the different centers are taken into consideration. Relative changes evolved by such additional absorption bands are mathematically calculated on the basis of the ligand theory, when the absorption centers are in the near ultraviolet; practically, Ti^{4+} and V^{5+} ions are prevailably to be recommended for such centers. They bring about an increase in the relative dispersion $\vartheta_{gF'}$ (for the wavelengths g and F′, respectively) which can then be applied for a controlled adjustment to the near-F' ultraviolet spectra of the special glasses concerned, when the matrix glass, as such, may have a lower absorption in this range. When the conditions in the near-infrared are examined, one will find (as a first approximation) after the insertion of an additional absorption agent, an increase in the absolute partial dispersion as a function of built-in additional centers, whereas $\vartheta_{gF'}$, in this case, will decrease.

335. Glasses with a high positive deviation of the relative partial dispersion $\nu_{gF'}$ from that of the matrix glass may be obtained either by a reduction of the absorption band in the near infrared by a shift of a preexisting band to longer waves, or by insertion of absorption bands in the near ultraviolet, when the glasses have a high negative deviation of the relative partial dispersion from that of the matrix glass. The practical verification of these ideas is possible either by *doping* the matrix glass with Fe_2O_3, TiO_2, or V_2O_5, or by *irradiation* with X-rays of 150 keV, as shown for Ag^+ ions containing phosphate glass to create Ag^0 centers thus inducing a shifting of absorption bands. Other experiments concerned crystalline alum, or fluorite, a few boro-

[151] Congr. Reports, Int. Camera Congr., 3rd, Prague, 1969, pp. 68–79.

[152] *Glastech. Ber.* **45**, (1), 1–9 (1972).

silicate glasses, and a fluorophosphate (E) glass as a matrix material. From a number of diagrams to show the "shifted spectra" effects, we have selected Figs. 94 and 95. It can be predicted that in the practical application of the effects described by Käs the doping by Ti^{4+} and V^{5-} is most promising, whereas, for Fe^{3+} the unavoidable reduction–oxidation reactions are troublesome; also, the X-irradiation methods meet difficulties for a controlled modification in Ag^{+}-containing glasses.

336. We may, for a complete analogy, immediately add a brief review of most recent advances in the evolution of *chalcogenide glasses* of which we reported other aspects (in ¶ 9 ff. 858–880). In order to avoid unnecessary repetitions, we mention

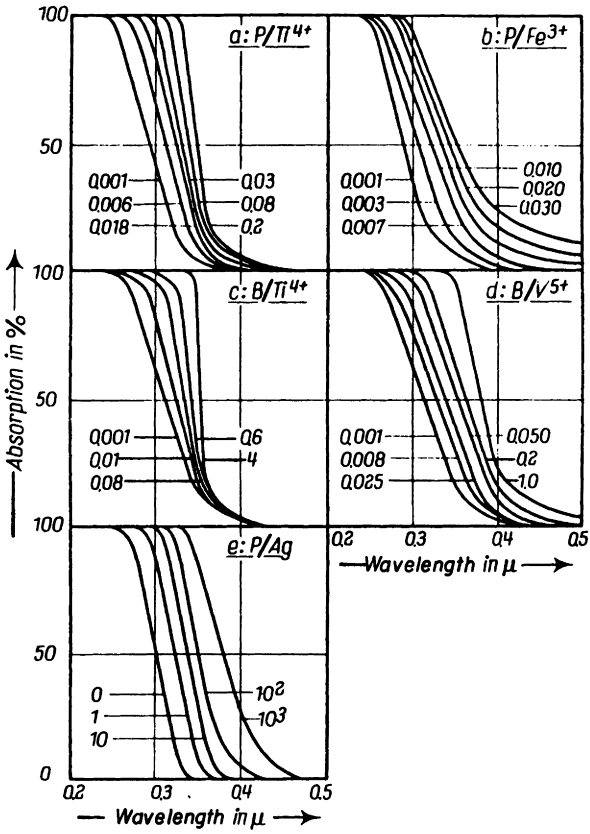


FIG. 94. Ultraviolet absorption of different glasses doped with TiO_2, Fe_2O_3, or V_2O_5, namely (a) alkali-aluminophosphate glasses doped with 0.001 to 0.200 wt. % TiO_2; (b) the same, doped with 0.001 to 0.030 wt. % Fe_2O_3; (c) alkali alumino-borate glass doped with 0.001 to 4.00 wt. % TiO_2; (d) the same doped with 0.001 to 1.00 wt. % V_2O_5; (e) silver-activated phosphate glass, irradiated with X rays 150 keV, for 0, 1, 10, 10^2, 10^3 minutes. (Käs.)

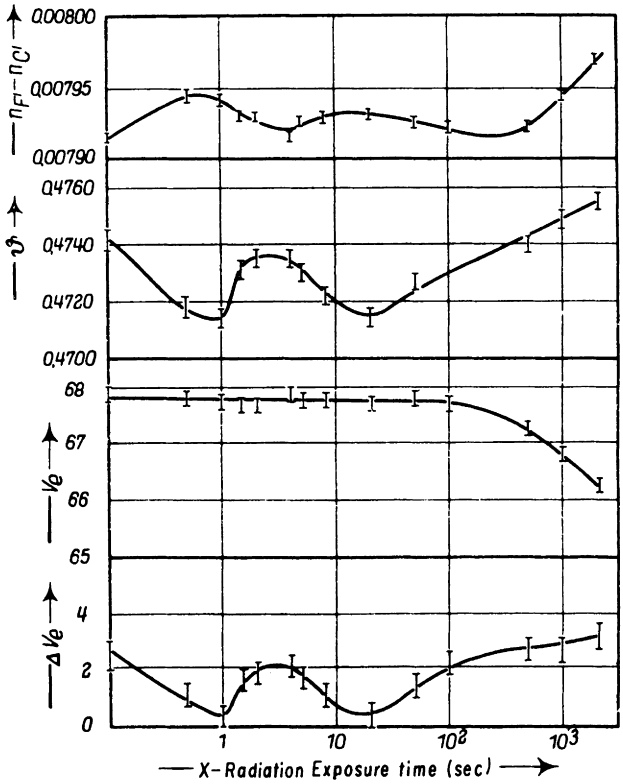


FIG. 95. Changes in the refractive index difference $n_{F'} - n_{C'}$, $\zeta_{g,F'}$, V_e, and ΔV_e (deviation from the norm line in V_e units), for a silver-activated phosphate glass as a function of the irradiation with X rays (150 keV). (Käs.)

here only some literature that may give information on technological applications or is of general interest from the viewpoints of glass science.

337. First, we mention a series of publications by J. D. MacKenzie[153] which are chiefly based on previous investigations of A. R. Hilton *et al.*[154] on new glass types, concerning besides chalcogenides, oxyhalogenides, and semiconducting oxide glasses of the vanadates (on system V_2O_5–P_2O_5, see Vol. VII. ¶ 20). Another orienting contribution by MacKenzie[155] covers more recent developments of special glasses with higher insulating quality for the glass films which are used as the substratum for thinnest electric wire-work, electronic conductant glasses, targets for image trans-

[153] Glass Ind. **47**, (Sept.), 488–493 (1966), with important literature bibliography.

[154] Cf. VII ¶ 525 f., 860.

[155] *Electronics* **39**, (19), 129–136 (1966).

mitter tubes, glass-ceramics with ferroelectric and ferromagnetic properties, phototropic glasses for information storage, photoconductors for xerographic purposes, so-called "dipping" chalcogenide glasses, and many other detailed applications. In the last-mentioned article, MacKenzie mentions advances made in the development of the new glass-bonded composites, with crystalline insulators, mostly of the mica family (natural, or synthetic, cf. "Mycalex," Vol. VII. ¶ 222). This latter group of composites is described in another article,[156] with emphasis on semiconductor-type binders, to avoid polarization electrostatic charges building up when ionic conductant insulator glass binders are used. Semiconductors, on the basis of *vanadates*, are an excellent example for such advanced, also hot-pressed and Mycalex-similar industrial products (ratio of mica:binder glass varying from 1:1 to 1:3).[157]

338. A highly detailed publication by A. R. Hilton, C. E. Jones, and M. Brau[158] orients on the glass-forming composition ranges for chalcogenide glasses in the basic systems, their properties, and from a highly important viewpoint, the study of possibilities for detecting and eliminating contaminations of those glasses by oxides. Detection is most possible with infrared spectroscopy as described by Hilton *et al.* The series finishes with discussions of the structural particularities of the glasses (cf. VII. ¶ 860). Possibilities for an application of dielectric coatings on chalcogenide glasses are to be examined, in order to avoid losses in reflectivity in the infrared range, as disclosed by Hilton, Brau, and Jones.[159]

339. For the wavelength range from 2 to 25 μ highly useful chalcogenide glasses could be developed in the systems Ge – As – Te and Ge – Te; an undesirable impediment for their use, however, is the very low softening temperature (270° and 380°C, respectively). It has not yet been possible to raise the softening points, e.g., by the substitution of Ge by tin; nevertheless, on Si – As – Te glasses, Hilton and Brau (1963) observed softening points near 500°C. Further improvement took place when Si and As were replaced by 5% Sb.[160]

J. A. Savage and S. Nielsen[161] studied the glass chalcogenide systems and learned that the glass formation range for Ge – As – Te glasses glasses could be widened by introduction of small amounts of silicon (up to 5 at %) (cf. Vol. VII. ¶ 876, 878).

[156] *Bull. Amer. Ceram. Soc.* **45**, (5), 539 f. (1966).

[157] On vanadate glasses and the V_2O_5–P_2O_5 system cf. VII. ¶ 20, and MacKenzie, *Umschau* **67**, (8), 263 (1967).

[158] *Phys. Chem. Glasses* **7**, (4), 105–112 (1966); **7**, (4), 112–116 (1966); **7**, (4), 116–126 (1966) **9**, (5), 148–152 (1968).

[159] *Infrared Phys.* **3**, (2), 69–76 (1963); **6**, 183–194 (1966).

[160] On the physical-chemical constitution of such glasses, see also VII. ¶ 879.

[161] *Phys. Chem. Glasses* **7**, (2), 56–59 (1966).

340. E. Plumat[162] (cf. Vol. VII. ¶ 861) investigated special glasses of binary and ternary *sulfide systems* and their chemical and physical properties (e.g., the "quasi-isomorphism" of such sulfides with corresponding oxides and their systems, and their analogous tendencies for unmixing reactions in the liquid state). The ionic conductivity of sulfide glasses (valid, of course, for corresponding selenides) containing alkali sulfides make their practical application as semiconductors not promising, in spite of many attractive results in Plumat's extensive experiments in this interesting field, not to speak of instabilities in a moist surrounding.

Another special investigation of glass semiconductors for heat conductance properties, was performed by I. A. Rozov, A. F. Chudnovskiĭ, and V. F. Kokorina[163] with As selenide and telluride glasses into which Ge and lead could be introduced (cf. VII. ¶ 879).

CRYSTALLIZATION TENDENCIES IN GLASSES

341. In the present Chapter dedicated to correlations between the properties of glasses in their chemical composition, we mentioned repeatedly the rather complex behavior of nucleation and crystallization (devitrification) which, however, is an extensive integral portion of Volume III.A of our series on silicate science. Nevertheless, the kinship existing between the tendencies for a transition from the liquid state into crystalline phases corresponding in case after case to the thermodynamic constellations of phase reactions justifies our saying from the aspects of practical opportunities and experience in the glass plant, a few words in the present Chapter. We see in a special Symposium organized by the American Ceramic Society in 1962[164] an article by J. M. Ohlberg, H. R. Golob, and D. W. Strickler[165] with very instructive observations and electron micrographs of material nucleated from titania-containing glasses of the systems $MgO-Al_2O_3-SiO_2-TiO_2$; $Li_2O-CaO-SiO_2-TiO_2$; $Li_2O-MgO-Al_2O_3-SiO_2$; which all belong to glass-ceramics materials, as important for this branch of modern manufacturing (cf. Vol. III.A. ¶ 39 ff.) and therefore mentioned repeatedly in our present text (¶ 321, 323). Internal nucleation, as here described in the early states is acting when crystallization begins at boundary interfaces glass/glass (one glass dispersed in the other by tendencies for unmixing, and so-called "droplet/matrix" evolution), and advances until microscopically visible crystallites and spherulites or the like are growing.

[162] Silicates Ind. **32**, (3), 125–134 (1967); *J. Amer. Ceram. Soc.* **51**, (9), 499–507 (1968).

[163] *Fiz. Tekh. Poluprov.* **1**, (8), 1159–1163 (1967).

[164] Symposium on Nucleation and Crystallization and Melts, Columbus, Ohio, 1962 (*Amer. Ceram. Soc.*) 123 pp.

[165] Reference 164, pp. 55–62.

342. We spoke in ¶ 311 and 327 of observations made by M. A. Matveev and Yu. M. Solodukho on the influence of titania as a typical and energetic nucleator agent in melts for manufacturing of glass–ceramics, to try avoiding the application of boric acid for the production of high-durability fiber glass (in view namely of economic difficulties existing for processing B_2O_3) for such a quality glass in the USSR. Alkali-free glasses of the system $MgO-CaO-Al_2O_3-SiO_2$ were proved to be highly satisfactory in chemical durability when the desirable high quality was reached by this B_2O_3-free product with a crystallization temperature between 1125° and 1200°C as the upper limit of the operation interval. An addition of only a moderate amount of SrO to the glass composition, as indicated above, acted also favorably even by reducing the tendencies for a spontaneous crystallization, not to speak of other desirable physical properties of the products (cf. Vol. VII. ¶ 537). Therefore, such glasses must be very promising for general use in fiber and glass wool products used for applications in the building construction industry, beyond notable economic savings.

343. The practical interest in borosilicate glasses for all kinds of technological applications has occupied attention for a long time, specifically for the "boric acid anomaly" which they show as a function of composition. For "Nabal" glasses, which are typical aluminates in composition, technological attention is focused on the phenomenon of inner friction and the thermal expansion reactions increases in temperature. H.deWaal[166] observed the boric acid anomaly in the experimentally established minimum of thermal expansion as a function of Na_2O and Al_2O_3 contents in the glass composition. We discussed in Vol. VII. ¶ 438 that the $[AlO_4]$ groups in Nabal glasses are fully exchangeable in both directions against $[BO_4]$ units in the glass constitution. Refined measurements, however, make it evident that certain deviations from this regularity may occur which are explained by the tricluster theory of E. D. Lacy[167] and are in agreement with the phenomena concerning the anomalies of inner friction.

344. It is technologically interesting that the constitution of non silicates rules the crystallization phenomena. M. M. Layton and A. Herczog[168] describe glasses of titanates and niobates, all of the crystallochemical type of perovskite as having a surprisingly good transparency when they reach full crystallization, when the crystallite sizes remain very low, even at the end of the devitrification process, and when the content of framework-forming constituents in the matrix glass is low. The conditions for such a nearly extreme crystallization phenomenon postulate an exceed-

[166] *Phys. Chem. Glasses* **10**, (3), 101–107 (1969).
[167] Cf. VII.A. ¶ 228, 237.
[168] *Glass Technol.* **10**, (2), 50–53 (1969).

ingly high number of spontaneous nucleation centers, and must evidently have an optimum ratio of the amounts in framework-forming and framework-modifying cations in quite definite limits as it is shown schematically in Fig. 96 (see more details in Vol. III.A. ¶ 39 f.), but based on silicate glasses with about equal amounts of atoms from the Groups IV.b., V.b., and I–II of the Periodic System of Elements. In this case, it is also essential that under quenching the glass should remain homogeneous, and not be separated into two liquid phases. This is believable from the diagram showing the extension of the original composition with increasing cooling rates, but changes in crystallization as a function of both parameters combined.

345. In the model glasses of the system Rb_2O-TiO_2 and Cs_2O-TiO_2, H. Marfels[169] showed a coexistence of glass and crystalline phases (Vol. VII. ¶ 409, 413).[170] Crystallization is particularly rapid in glasses of dititanate composition (on the crystallization of glasses containing ThO_2, and rare earths like La_2O_3 and Tb_2O_3, see also R. Katzschmann,[171]); not more than 1% Al_2O_3 are tolerated.

DIELECTRIC PROPERTIES IN CORRELATION WITH CRYSTALLIZATION

346. Crystallization of lead aluminosilicate glasses containing niobates, were described by R. C. Anderson and A. L. Friedberg[172] and are of particular interest because of the appearance of pronouncedly *ferroelectric* semiconductors, e.g., of $PbNb_2O_6$ (in three modifications), a rhombohedral and an orthorhombic form being most important as primary crystallization products. The dielectric constants, loss factors, and other parameters were measured extensively making understandable why the dielectric constants are sometimes "washed out" by polymorphic inversion effects, although the X-ray diffraction analysis did not give a clear confirmation of such an assumption. Maxima in dielectric constants would not exactly define a ferroelectric response near the Curie temperature of about 570°C for the orthorhombic modification. This is an impressive example of the fact that interfacial effects of polarization and electron trapping in high-energy positions depend greatly on the thermal treatment for more or less rapid cooling effects. Electron migration should provide a false rise in the dielectric constant and the dissipation factor only on heating.

[169] *Glastech. Ber.* **42**, (5), 161–176 (1969).

[170] See also ¶ 210 on clustering and immiscibility phenomenae, and J. Bh. V. J. Rao's observations of titanate glasses, *J. Amer. Ceram. Soc.* **47**, (9), 455–463 (1964); cf. ¶ 318.

[171] *Glass Technol.* **6** (5), 156–160 (1965).

[172] Symp. on Nucleation and Crystallization of Glasses and Melts, Columbus, Ohio 1962, *Amer. Ceram. Soc.*, pp. 29–34.

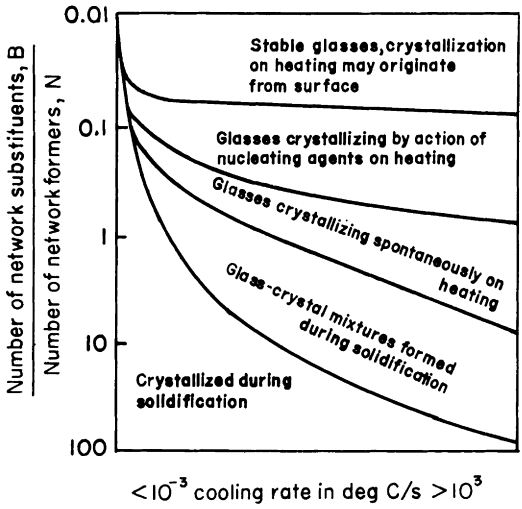


FIG. 96. Structure and crystallization behavior of oxide systems formed by solidification. (Layton and Herczog.)

347. In this connection, Ch. Hirayama and D. Berg[173] examined similar problems for glasses of the system $Na_2O-Nb_2O_5-SiO_2$ (with 9.5 to 41.5 mole % Nb_2O_5), combined with studies of the dielectric constants as a function of frequencies (between 100 and 10^{10} Hz). In the sodium niobate glasses, the experimentally measured very high dielectric constants, like the density, are evidently a consequence of the small ionic radius of Nb^{5+} and the high electrostatic charges, which make this type of glass so very interesting from the viewpoint of technology of electronics. Such is the case too, for the corresponding titanate glasses of which we spoke before (cf. H. J. L. Trap and J. M. Stevels).[174]

348. Only briefly may we mention measurements of the dielectric constant and of tan δ values determined by T. V. and V. A. Dubovik,[175] with TiO_2-containing alkali-alkaline earth-aluminosilicate glasses (also the same, with ZnO added) which, with a systematic increase in the ionic radii of the alkali cations, show a decreasing temperature correlation with dielectric constants and losses. Furthermore, we refer to corresponding measurements of dielectric properties of aluminosilicophosphate glasses made by R. Y. Berzin, T. N. Miller, and A. Ya. Vaĭvad,[176] who demonstrated

[173] *J. Amer. Ceram. Soc.* **46**, (2), 85–88 (1963).

[174] *Phys. Chem. Glasses* **1**, (4), 107–118 (1960).

[175] *Izv. Akad. Nauk S.S.S.R., Neorgan. Khim.* **2**, 1827–1831 (1966).

[176] In the book "Glass-Forming Systems and Materials," (Yu. Ya. Eĭduk, ed.), pp. 179–182, Zinatne, Riga, 1967.

how the substitution of CaO by BaO increases the dielectric transmittancy (for a frequency of 50 Hz), but reduces the increase in tan δ with rising temperature. E. Zh. Freĭdenfel'd, Z. P. Milberg, and T. P. Riekstin[177] have made corresponding measurements for a series of glasslike compositions $0.8Na_2O$, 0.2 CdO, Nb_2O_5, and 0.5 Na_2O, 0.5 K_2O, Nb_2O_5, to study the crystallization of Seignette-salt-type compounds at 730°C, partly also with the introduction of Ta_2O_5 and SnO_2. The crystalline phases thus produced had a Curie temperature of about 360°C.

349. A much simpler glass of the system $R_2O-RO-PbO-SiO_2$ was studied by M. Mikoda, T. Kuroda, and Sh. Hayakawa,[178] in its crystallization behavior and dielectric properties, to learn how the initially existing conditions of matrix material with a relatively low dielectric loss are changed systematically in tan δ as a function of thermal treatment, in parallelism with starting nucleation and crystallization. For low frequencies and with increasing temperature, the electric resistance and the activation energy of conductivity decrease, but an increase in the loss angle is most characteristic. From these effects, it is evident how thermal treatment progressively enriches the alkalies in the residual matrix glass, whereas, the devitrification products being progressively enriched, e.g., in the crystalline $PbO \cdot SiO_2$ identified by X-ray diffraction analysis. The stronger chemical bonding develops, thus decreasing deformation losses and dissipation factors.

350. $NaNbO_3$, as the crystalline phase of glass in the concentration range from 18–33 mole % SiO_2, 41–33 mole % Na_2O, and 41–33 mole % Nb_2O_5, was prepared by the very sudden quenching of the molten composition. The crystallization was very rapid and accompanied by a strong exothermic heat evolution in experiments of M. M. Layton and A. Herczog[179] (cf. later in Vol. III.A. ¶ 39 f.). A striking transparency of the fully crystalline products (cf. ¶ 344) is a consequence of smallest individual crystallites of $NaNbO_3$ in the order of magnitude from 200 to 10,000 Å in diameter, depending on the silica content of the initial glass melts. An increasing opacity also observed depends mostly on a simultaneous crystallization of high-cristobalite during the thermal treatment of samples. We recall in this connection other observations made by M. Monneraye, J. Serindat, and C. Jouwersma[180] on glass-ceramics during the crystallization of rutile and $SrTiO_3$-doped glasses of the Cabal type, concerning dielectric properties like the permittivity and its temperature coefficient, power factor, and dielectric losses. High losses occurring in the glass-ceramics prepared from such glasses, are caused by the nonstoichiometry of the

[177] Reference 176, pp. 183–187.
[178] *Bull. Amer. Ceram. Soc.* **46**, (5), 539–542 (1967).
[179] *J. Amer. Ceram. Soc.* **50**, (7), 369–375 (1967).
[180] *Glass Technol.* **9**, (3), 70–77 (1968).

crystalline phases as could be demonstrated when doping was done with Cr^{3+} or Ta^{5+} ions (cf. Vol. III.A. ¶ 39 ff.; this volume ¶ 323).

351. Of great interest may be a publication by V. N. Golukhin, M. V. Zimina, R. P. Smirnova, and L. A. Solov'eva[181] on the crystallization tendencies of *gallium*-containing glasses of the systems $Na_2O-Ga_2O_3-B_2O_3-SiO_2$ and $PbO-Ga_2O_3-B_2O_3$. The glass formation range of the last-mentioned silica-free system is surprisingly large, much wider than any known from the corresponding ternary systems containing rare-earth oxides like $PbO-La_2O_3-B_2O_3$. This difference in the glass characteristics is also valid for the optical qualities: gallium-containing glasses have better developed properties of the flint glass type than are known for the La_2O_3-containing glasses of corresponding composition.

352. Even the classical system $Na_2O-BaO-SiO_2$ was recommended by P. W. L. Graham, L. E. Cross, and G. E. Rindone (cf. Vol. VII. ¶ 264)[182] in its dielectric permittivity and loss behavior over the composition series $(1-x)\,Na_2O;\,x\,BaO;\,2.00\,SiO_2$, for the frequencies range from 10^2 to 10^5 Hz. The large changes observed in the dielectric losses associated with the relaxation were tentatively interpreted in the formulation of the Maxwell–Wagner theory. Although the dielectric losses are caused in both cases by mechanical *and* electric losses by the Na^+ ions, the relaxations follow different mechanisms; one cannot take it for granted that in every case there is a mechanical relaxation known which would be strictly equivalent to the Maxwell–Wagner model concepts.

ELECTRICAL PROPERTIES AT LOW TEMPERATURES; GLASS ELECTRODES

353. The task of this present chapter cannot be a thorough physical-chemical basis for a handbook article on glass electrodes or in the style of M. Dole's classical book[183] but wishes only to present the reader with a rapid orientation of some recent advances in this important field. We start our report with the necessary recommendation that the reader make himself familiar with the very complete contribution that G. Eisenman made with publications of his work, and then with his extremely valuable new handbook.[184] The first Section is devoted to a comprehensive analysis of

[181] *Zh. Prikl. Khim.* **41**, (7), 1447–1452 (1968).

[182] *Phys. Chem. Glasses* **10**, (6), 217–221 (1969).

[183] "The Glass Electrode," Wiley, New York, 1941.

[184] E. Arnold and M. Dekker, "Glass Electrodes for Hydrogen and other Cations. Principle and Practice," 555 pp. London and New York, 1967, with more than 1000 literature references; the review by A. K. Covington, *Phys. Chem. Glasses* **9**, (1), 36, (1968), is particularly instructive as an introduction and a rapid survey of the organization and contents of this most valuable book.

the theory of all kinds of cation-sensitive glass electrodes, with special representation of the pH electrodes. The reader may also familiarize himself with the principles and practice of construction. Among single contributions, we emphasize those of J. O. Isard on the chemical composition of glass electrodes, of R. H. Doremus on diffusion potentials, and of B. P. Nikolsky and M. M. Shultz on ion-exchange potentials. G. Mattock[185] discussed, in addition, the correlation of electrode glasses and their function as dependent on their chemisms. Of greatest importance then in Doremus' and Eisenman's report on phase boundary and diffusion potentials, whereas Nikolsky and Eisenman discuss the chemistry of glass in its function as active membrane material.

354. From a more practical viewpoint, a review by H. D. Portnoy describes such modern special electrode developments as cationic aluminosilicate electrodes, and one by A. H. Truesdell and A. K. Covington as a contribution on Ca-selective electrodes. The practical application to problems of analytical chemistry which may be in the foreground of what Eisenman wishes to provide in his handbook and is represented by an article of G. A. Rechnitz and A. M. Pommer, includes a most fascinating report by R. M. Garrels on the estimation of activity coefficients for geochemical and pedological investigations on soil solutions which we discuss in Vols. IV.A. ¶ 453, 490 ff. and IV.B. ¶ 105 ff.

355. We must restrict our present text somewhat on the subject of Na^+- and Ca^{2+}-sensitive glass electrodes and their potentials, but for an important application of fundamental questions in silicate research, we enumerate these few selected problems as follows:

G. Eisenman's studies on alkali-selective glass electrodes, and their modes of operation,[186] and their application for mineralogical and pedological purposes in general may serve for an introduction.

R. M. Garrels, M. Sato, M. E. Thompson, and A. H. Truesdell[187] discussed in a more general way the sensitivity of glass electrodes to divalent cations, in the same way that R. M. Garrels and P. B. Hostetler[188] did for the transportation and precipitation of uranium and vanadium from soil solutions inducing the important enrichment of sandstone-type sediments with these elements.[189] Truesdell also described the geochemistry of glass weathering in principle as being determined by base exchange

[185] "pH Measurement and Titration," McMillan, New York, 1961.

[186] *Biophys. J.* **2**, 259–323 (1962).

[187] *Science* **135**, 1045–1048 (1962).

[188] *Econ. Geol.* **57**, 137–167 (1962).

[189] See also A. H. Truesdell, *Geol. Soc. Amer., Spec. Paper* **76**, 170 (1964); cf. IV.B. ¶ 98, footnote 186.

problems which could be investigated as demonstrated, for a series of natural glasses with silica contents of 45.2 to 97.0 wt% by electrode glass methods which have a specific selectivity sequence $2H^+ > 2K^+ > 2Na^+ > Ca^{2+} > Mg^{2+}$. Although omitting literature of purely analytical character, we mention here a development of an excellent selectivity of alkaline earth cations in studies by A. H. Truesdell and A. M. Pommer[190] that are suitable for activity determinations of Ca^{2+} in a *phosphate* glass with the sequence $2H^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > 2K^+ > 2Na^+ > Mg^{2+}$ in natural systems in which Mg^{2+} widely occurs.

356. As one example for the excellent suitability of glass electrodes for investigations on *tectites* A. H. Truesdell[191] presented a curve showing how additions of Ca^{2+} ions to a solution of 10^{-3} mole KCl ($\log K' = -3.016$), follow the equation for the electromotive force of the type

$$E = C_A + \frac{RT}{2F} \ln \frac{[A^+]^2}{\lambda_{A_2X_2}} + K_{AB} \frac{[B^-]^2}{\lambda_{B_2X_2}}$$

given by Garrels (1962)[192]. H. Dutz[193] developed another glass electrode indicating activities of highly dilute to concentrated solutions of sodium salts, directly, and continuously. Specific influences of other cations like K^+, NH^+, Cs^+, and Ca^{2+} in such systems must be corrected. Combined measurements of NH_4^+, H^+, and Na^+ glass electrodes make it possible to decipher the mechanisms of their exchange on phase boundaries from solution/swelling layers.

357. The problems of cation-sensitive glass electrodes were studied by J. A. Savage and J. O. Isard[194] for compositions of the systems $Li_2O - Al_2O_3 - SiO_2$; $Na_2O - B_2O_3 - SiO_2$; $Na_2O - Al_2O_3 - P_2O_5 - SiO_2$, the potentials of which were measured in alkali salt solutions for a determination of the constant K in Eisenman's equation. Lithium silicate solutions are singular in their constitution-determined electrode properties insofar as the anion sites have a higher field potential than corresponding ones in other glasses. The Na borosilicate glasses are more sensitive to H^+ ions than are Na aluminosilicate glasses. When P_2O_5 is introduced into the composition of Na aluminosilicate glasses, the selectivity for alkali ions remains intact, but in $Na_2O -$

[190] *Science* **142**, (3597), 1292–1294 (1963).

[191] A. H. Truesdell, *Amer. Miner.* **51**, (1/2), 110–122 (1966).

[192] See in Garrels and C. L. Christ, in "Minerals Solutions and Equilibria," Harper, New York, 1962.

[193] *Glastech. Ber.* **39**, (3), 139–140 (1966), with valuable literature information on the preparation of Na^+ sensitive glass electrodes on the basis of sodium aluminosilicates, with relatively high fusion temperatures.

[194] *Phys. Chem. Glasses* **7**, (2), 60–67 (1966).

TiO_2-SiO_2 glasses, the selectivity is decidedly lower. Anomalies in the indications of glass electrodes by a slow "drifting" are chiefly caused by changes in the hydration degree of membrane glasses. Another troublesome anomaly is the interference of adsorption phenomena by the formation of pronounced double layers on the surface of the electrode glass. However, Savage and Isard finally came to the conclusion that such irregularities cannot cause greater trouble than local disturbances, and cannot affect the decisive potential steps ($\psi' - \psi^+$) in Fig. 97, when equilibrium has been established.

358. Interesting glass electrode properties are described for complex Na vanadate–silicate glass compositions by E. A. Ivanova, A. A. Belyustin, and M. M. Shul'ts.[195] Such glasses contain a framework-forming, a framwork-modifying, and an intermediate element, all at the same time. When Ba^{2+} is introduced as a

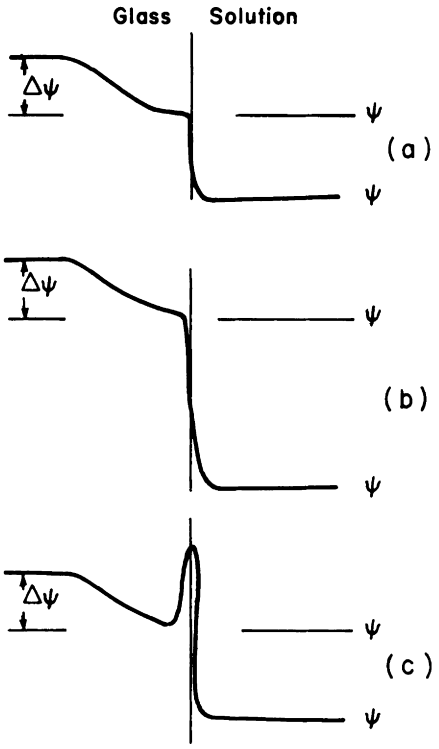


FIG. 97. Schematic potential distribution at glass-solution boundaries: (a) without absorption at surface sites; (b) with surface absorption before equilibrium is reached; (c) with surface absorption after equilibrium is established. (Savage and Isard.)

[195] *Zh. Prikl. Khim.* **39**, (12), 2527–2532 (1966).

framework-modifying cation, a neutralization of ionizable groups may take place. Another milder neutralization effect is observed when Mg^{2+} cooperates as an intermediate cation. Such changes in the chemical composition of (2%) Al- and (2%) V-α containing Na silicate glasses react rather sensitively in their potential properties. Analogous studies by the same authors[196] concern not only the electrode properties but also the magnetic susceptibility and the absorption spectra when the Na silicate glasses are modified by introduction of V_2O_5 and Nb_2O_5 which bring about multiple variations in those parameters by changes in the cation valencies and coordination configurations, with ensuing glass electrode characteristics.

359. In fundamental studies on the determination of mean activity coefficients, γ_2, of salts, single or in mixtures, P. B. Hostetler, A. E. Truesdell, and C. L. Christ[197] constructed a galvanic electromotive force cell of the following type:

		(without a liquid junction)
K^+ sensitive glass electrode, Beckman No. 39137	KCl solution (0.015, to 1.00 molar)	Ag|AgCl electrode, prepared by electrolytic deposition of AgCl on Ag

360. A. K. Covington and T. H. Lilley[198] examined the response of Ag^+ ions with different Na aluminosilicate glasses by direct comparison with the Ag electrode (in solution of silver nitrate concentration 1.00 to 0.0001 molar) at constant pH. The cell which was used was

Ag	$AgNO_3$	Glass 0.1 *N* HCl solution	AgCl	Ag

The first result was rather inconclusive, since little or no response of the Ag^+ ions to the glasses was observed although, on the other hand, they responded well to Na^+ ions. A commercial glass electrode (B. H. 104) of Na^+ sensitivity, however, gave a nearly theoretical response to Ag^+ ions. An even better response than that by B. H. 104 was shown by a Li aluminosilicate B. H. 68[199]; furthermore, A. L. Budd[200] found a higher Ag^+ sensitivity in the Li aluminosilicate glass (Beckman) No. 39278, than for H^+ ions, but found inverse effects with a Na aluminosilicate glass No. 39137. The glass anomaly is shown by Fig. 98.

361. G. A. Rechnitz and G. C. Kugler[201] examined the time-dependent changes in electromotive force for two cation-sensitive glass electrodes with the remarkable

[196] *Zh. Prikl. Khim.* **39**, (11), 2335–2341 (1966).
[197] *Science* **155**, (3769), 1537–1539 (1967).
[198] *Phys. Chem. Glasses* **8**, (3), 88–91 (1967).
[199] G. Mattock, 1961, "pH Measurement and Titration," McMillan, New York, 1961. pp. 406.
[200] *J. Electroanal. Chem.* **5**, 35 (1965).
[201] *Anal. Chem.* **39**, 1682–1688 (1967).

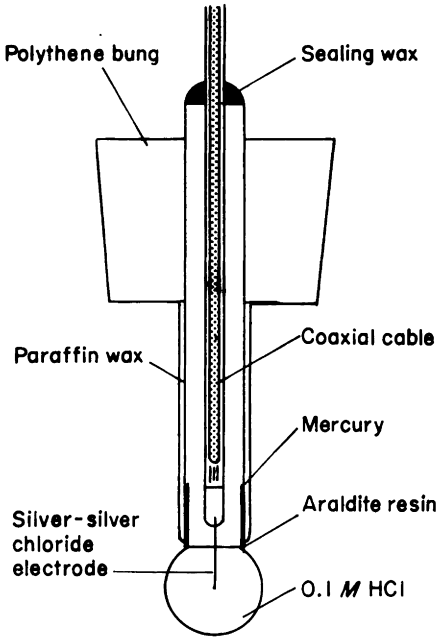


FIG. 98. Glass electrode assembly. (Covington and Lilley.)

result that for extremely short time periods, the electrical characteristics of the electrode rule the rate of reaction, whereas, for binary mixtures, it is slower in response. In the opinion of the authors, this is typical; one cannot determine the speed of the single processes with higher degrees of accuracy with glass electrodes directly.

362. That the evolution of highly alkali-sensitive particularly Na^+-sensitive, glass electrodes is not yet come to a satisfactory end, may be seen from the note by J. Stefanac and W. Simon[202] who prepared such electrodes from a molten mixture of Li_2CO_3; $Al(OH)_3$, B_2O_3, SiO_2, and Ga_2O_3, in a platinum crucible at 1500°C, fulfilling the requirements for good glass electrode qualities.

363. Another group of publications includes observations made by J. E. McLure and Th. B. Reddy[203] on the responses of cationic glass electrodes to alkali ions in nonaqueous liquid media. J. P. Adloff, G. Goldstein, and J. P. Schwing[204] reported

[202] *Anal. Lett.* **1**, (2), 1–9 (1967).
[203] *Anal. Chem.* **40**, (13), 2064–2066 (1968); cf. *Beckman Rep.*, No. 1, 36 (1969).
[204] *C. R. Acad. Sci.* **266**, (25), 1670–1673 (1968).

on deviations from the normal potentials of glass electrodes in the presence of glass-forming oxides which send ions into solution, e.g., when the electrode is dipped into a solution containing a molybdate- or wolframate- (tungstate) containing component. In the opinion of the authors, such an anomaly is manifestly caused by an ion-exchange reaction of that special type in which $[SiO_4]$ tetrahedral groups are exchanged by "foreign" coordination groups, $[XO_4]$.

364. Dynamic influences detected in changes of the response sensitivity of a given glass electrode with time and the working conditions, too, are observed and interpreted by G. Johansson and Karin Norberg.[205] Phenomena of this kind can be expressed in mathematical formulation and general equations.

365. Pyrex glass electrodes were described by R. A. Doremus.[206] Their potentials measured in molten salts ($NaNO_3$ + $AgNO_3$) showed a satisfactory agreement with the theory of ionic exchange reactions for membrane electrodes, and for determinations of ionic distribution and mobility in Pyrex glass. The same author[207] measured electrical potentials on silica glass and Vycor in molten salt mixtures (Na and Ag nitrate, see above), and applied the data for a calculation of mobilities and preference, which thus confirm the postulates of a general ion-exchange theory which is also valid for the glass electrodes.

366. A. K. Covington, Maya Paabo, R. A. Robinson, and R. G. Bates[208] made the experimentally important observation that commercial glass electrodes can stand application in *heavy water* (D_2O) in the same manner as they are used in H_2O. This result is of great importance for application in a correlation between the standard data of the pD (p_aD) scale, with increased pH data, in heavy water.

367. As R. C. Knupp[209] could demonstrate that it is possible to use commercially available Na^+- and Ca^{2+}-sensitive glass electrodes quantitatively to determine the occurrence of acid-soluble Na^+ and Ca^{2+} sources in glass *batches*. The reproductiveness of the measured potentials equal ±0.53 mV standard deviation for the Na^+ electrodes, ±0.62 mV for the Ca^{2+} electrodes, corresponding to a precision of ±0.40% Na_2CO_3, and ±.72 mV for the limestone contents in the glass batches. The possibility of a control of batch compositions in this way is illustrated by Fig. 99 which shows results of electroanalytical batch examination with deviation data from main averages (as ±% in the batches) for soda and limestone.

368. Another most fascinating practical problem arising in the surface layers of

[205] *J. Electroanal. Chem. Interfacial Electrochem.* (*Lausanne*), **18**, (3), 239–250 (1968).
[206] *J. Electrochem.* **115**, (9), 924–927 (1968).
[207] *J. Phys. Chem.* **72**, (8), 2877–2882 (1968).
[208] *Anal. Chem.* **40**, (4), 700–706 (1968).
[209] *Bull. Amer. Ceram. Soc.* **49**, (9), 773–776 (1970).

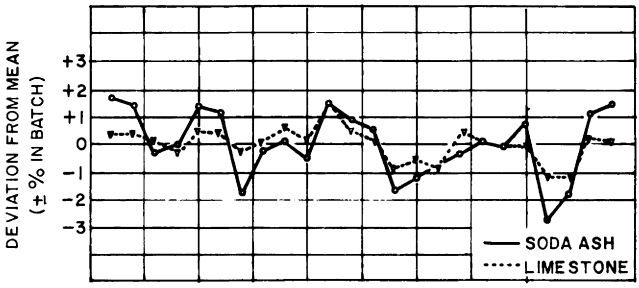


FIG. 99. Typical recorded electroanalyzed batch results. (Knupp.)

leached "swollen" glass electrode membranes (containing Li^+ ions) is discussed in a recent report by H. Bach and T. G. K. Baucke,[210] with detailed consideration of the adsorption potential, the membrane potential, the statistical-mechanical theory, and the phase boundary or ion-exchange theory. The last, the most widely accepted, is based on the classical Nernst theories of potential differences at liquid/solid electrolytes (1892). It can satisfactorily describe the concentration dependence of the potentials and the so-called alkali and acid errors.[211] We cannot detail here the existence and role of a "gel layer" or a "swollen surface layer" which is the colloid-physical phenomenon combined with water imbibition by the membrane and ion exchange (cf. ¶ 380). Much too little is known of its structure, and no clear definition is available of the concentration profiles of ions within the surface layer of glass electrodes. Therefore, new ways must be found to solve this complex problem. Bach and Baucke, contributed under different aspects, working on the problem with experiments on the luminescence responses of surface layers, (Vol. VII. ¶ 788, footnote 4). K. Schwabe and H. Dahms suggested radioactive tracer methods[212] which, unfortunately, are not applicable to lithium-containing glass electrodes and membranes, since there is no isotope of Li^+ suited for this purpose (cf. Vol. VII. 104 ff.).

369. We add here brief references to some publications, chiefly of Russian authors. M. M. Shul'ts, N. V. Peshekhonova, L. M. Romanova, and A. A. Adrianov[213] observed wide changes in the electrode properties of Li aluminosilicate glass electrodes; changes in the chemical composition are explained by changes in the nature of the bonds between anions and protons in the glass structure, with excess in sites with

[210] *Electrochim. Acta* **16**, 1311–1319 (1971).

[211] Cf. K. Schwabe and H. Dahms, *Z. Elektrochem.* **65**, 518–526 (1961); **66**, 304–312 (1962).

[212] Cf. *Naturwissenschaften* **47**, (15), 351–352 (1960); *Isotopentechnik* **1**, 34–39 (1960).

[213] *Vestn. Leningrad. Univ. Ser. Fiz. Khim.* **17**, (16), (3), 108–115 (1962).

negative charges which bring out the pronounced dependence of the potentials as a function of pH.

370. V. S. Bobrov and M. M. Shul'ts[214] developed curves for the electromotive forces as a function of pH for a 23 mole % K_2O; 36 mole % P_2O_5; 40 mole % Al_2O_3 glass (containing only 0.8 mole % SiO_2) with two ionic groups of different acidity, one of related but even more complex phosphoaluminate and one of borophosphate type. They concluded that glass electrodes of these compositions have an H function combined with a metal function, and therefore can be applied for pH measurements in solutions for which silica-containing electrodes are not suitable.

371. M. M. Shul'ts, A. I. Parfenov, Te-Yu Ch'en, T. G. Bondarenko, and Yu. Ya. Mekhryushev studied the electrode properties of glasses of the system $Li_2O - Cs_2O - La_2O_3 - SiO_2$, and the correlation to binary and ternary partial system compositions. Interesting here, is the simple additivity of the electrode properties of Cs_2O and La_2O_3, whereas, the introduction of the low electrostatic charge of Cs^+ is combined with a stronger bonding of protons, in consequence of which the upper limit H^+ function is shifted into the alkaline range of the glass structure observed, thus causing deviations of this function into the anionic range making the glass unstable. On the other hand, La_2O_3 strengthens the structure, increases durability, and eliminates the deviations to the acidic side.

372. B. P. Nikol'skiĭ and M. M. Shul'ts[216] gave instructive explanations of the exchange theory of glass electrodes, and revise previous opinions,[217] by taking into consideration variations in bond strengths between the glass anions and Na^+ and/or H^+ cations. Furthermore, they calculated the potentials for glasses containing one or two anionic groups varying the different equilibrium constants.

373. The high degree of variability of electrode functions in a wide range of compositions suitable for the construction of glass electrodes is verified in publications by M. M. Shul'ts, with A. I. Parfenov, N. V. Peshekhonova, A. A. Belyustin, E. A. Ivanova, V. N. Petrova, T. A. Kopuntsova, and L. P. Shandalova.[218] Particular attention is given to systematic studies of the influence of alkaline earth cations on the potentials, and to detailed properties of standard electrode glass com-

[214] *Vestn. Leningrad. Univ. Ser. Fiz. Khim.* **18**, (4), (1), 166–171 (1963).

[215] *Vestn. Leningrad. Univ. Ser Fiz. Khim.* **18**, (4), (1), 155–160 (1963).

[216] *Vestn. Leningrad. Univ. Ser. Fiz. Khim.* **18**, (4), (1), 73–86 (1963); with A. A. Bel'yustin, **18**, (4), (1), 86–93 (1963).

[217] Cf. Nikol'skii and A. A. Zhdanov, *Zh. Fiz. Khim.* **27**, 724–743 (1953) and Nikol'skii and Shul'ts, *ibid.* **36**, 1327–1330 (1962).

[218] *Vestn. Leningrad. Univ. Ser. Fiz. Khim.* **18**, (4), (1), 98–104; (1963); **18**, (4), (1), 104–114 (1963); **18**, (4), (1), 114–120 (1963).

positions as seen from changes in the electromotoric forces as a function of pH conditions.

374. Titania-containing glass electrodes were studied by M. M. Shul'ts, V. S. Bobrov, and I. S. Bukhareva[219] on the basis of Li and Na silicate glasses, with particular emphasis on calculations of presumably relative amounts in Ti^{4+} coordination groups and that an alkalinization effect is to be ascribed when $[TiO_4]$ groups prevail, whereas, $[TiO_6]$ exert an acidizing action as seen from the potential curves versus pH.

375. A few additional lines may be dedicated to interesting observations made by A. E. Mans, and I. Kateman[220] on a (6%) *beryllium*-containing silicate glass electrode in its response behavior to other cations (with the exception of protons). The sequence of the monovalent cations is $H^+ > Ag^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+ > [C_3H_7(NH_3)]^+$.

376. Investigations on the *time* bound variations in the electromotive forces of glass electrodes were made by W. H. Beck, J. Caudle, A. K. Covington, and W. F. K. Wynne-Jones.[221] Pretreatments of the glass electrodes in a medium comparable to that for which they are determined in service, from case to case, reduce asymmetry potential changes and may also modify the characteristic patterns of the electromotive forces as a function of time variations, with different speed reactions.

377. The recent literature on glass electrodes is affiliated in such a remarkable way with facts and theories in the related field of *cation-exchange reactions*, that we cannot omit this correlation significance and must acquaint the reader with some publications coming from the school of M. M. Shul'ts a few of its most representative results of which we discussed in the preceding paragraphs. The group around V. V. Moĭseev has much special merit. Before enumerating a few other Russian papers, we emphasize an excellent review given by Moĭseev himself some time ago.[222] We start from investigations made by Moĭseev and V. A. Zhabrev[223] for a study of ^{22}Na in self-diffusion in Na disilicate glass, using the so-called "grinding" techniques based on a progressive measurement of profile diffusion from layer to layer in cylindrical samples (cf. Vol. VII. ¶ 118 ff.), with and without the participation of alumina in the glass composition, and indicated by systematic changes of the self-diffusion coef-

[219] *Vestn. Leningrad. Univ. Ser. Fiz. Khim.* **18**, (4), (1), 139–142 (1963).

[220] *Rev. Trav. Chim. Pays-Bas* **81**, 916–924 (1962).

[221] *Proc. Chem. Soc.*, 110–111 (1963).

[222] In Proc. Conf. Silicate Ind., 7th, Budapest, 1963, Vol. 7, pp. 55–61, Akadémiai Kiadó, 1965, specifically on the successful introduction of radioactive tracer methods.

[223] *Silicates Ind.* **30**, (9), 475–499 (1965).

ficient, suitable for the calculation of the Eyring theory of rate processes when applied to numerical data of the Na^+ ion diffusion in Einstein's diffusion equation.

378. The correlation of these self-diffusion and cation-exchange studies to direct measurements of the exchange equilibria under modifications by alumina was examined by T. M. Permyakova and V. V. Moĭseev[224] who talked of glass systems in contact with salts or other glasses of Li aluminosilicate composition type, demonstrating the strong decrease in the diffusion coefficient for Na^+ ions in the cation-exchanging system, with increasing concentrations of Al_2O_3. First experiments in this direction by J. Voldán[225] were followed by other studies on cation-exchange equilibria in aluminosilicate systems of the zeolite class (cf. Vol. V. B. ¶ 105 ff.). The calculation of activation energies for ion diffusion, e.g., for Na^+ ions in glasses made it quite evident that *not all* Na^+ participating in a glass structure is capable of diffusion, a small percentage (1.7 wt %) being presumably more firmly anchored in potential "troughs" of the framework—an observation of great importance for hydrothermal cation-exchange reactions of feldspar and feldspathoids in metasomatic rocks (cf. Vol. IV.A. ¶ 322).

379. Particularly interesting are such cation-exchanging reactions in *porous glasses*. They were studied by I. Altug and A. L. Hair[226] who applied a pH filtration method. The examination of the curves gave clear evidence that there are two different ranges of cation-exchange actions with different acidity reactivity (cf. Vol. II.B. ¶ 192). Porous glasses of Vycor type show another interesting "salt rejection" effect which is described by K. A. Kraus, A. E. Marcinkowsky, J. S. Johnson, and A. J. Shor[227] as a kind of filtration of salts (chlorides of Na, Ca, Mg, sulfates of Na and Mg). It becomes evident that salts with divalent co-ions (i.e., anions like SO_4^{2-}) reject more strongly than monovalent ions. The salts are withdrawn from aqueous solutions when passed through the capillary channels under pressure. This "rejection effect" is the better marked, the higher the pH value (up to pH = 10) of the solution; there is also a pronounced increase in the filtration effect when Th^{4+} ions are introduced into the solution.

380. From this instance it becomes convincing that the complex phenomena here simply called a "filtration" are, in reality, mechanisms in salt systems very closely related to energetic cation-exchange reactions. The percentage of rejection can thus be driven up to 70% when the pressure driving the solution through the channels

[224] *Izv. Akad. Nauk S.S.S.R., Neorgan. Khim* **3**, (10), 1916–1920 (1967).

[225] *Sklar Keram.* **9**, (1), 16–20 (1959), reviewed by G. Nickl and F. G. Wihsmann, *Silikattechnik* **11**, (12), 582–583 (1960).

[226] *J. Phys. Chem.* **71**, (13), 4260–4263 (1967).

[227] *Science* **151**, (3707), 194–195 (1966).

reaches 100 atms. The filtration of polyvalent cations by glasses of Vycor type is certainly more complex than would be a simple ion "exclusion" process; in this way, the surprising fact is that enrichment occurred with La^{3+} (nitrate as the "filtered" salt) which demonstrates that neither "exclusion" nor the Donnan-type rejection on membranes had taken place as is preferably used in electrodialysis or other reverse-osmosis phenomena applied in desalination.

381. Some practically significant phenomena which are observed with the polished surfaces of porous glass, although not precisely belonging to the effects of ionic selectivity in silicate glasses, can be treated like ionic membranes as M. L. Hair and I. Altug[228] described. Layers of such a surface-modified glass evidently reduce the initial porosity. The density of the membrane is, however, *in*creased, the selective response to alkali ions in the presence of Ca^{2+} ions increased too. The reduction of pore sizes, as observed in electron microscopic section samples and the measured surface compaction data, confirm the conclusion that during polishing a viscous flow phenomenon takes place as a consequence of local temperature-increase conditions which partly close the free cross sections. Experimentally, it has been possible to make evident the fact that the membrane potentials of the polished glass vary in different stages of manipulation and with use of different polishing agents (Fe_2O_3 rouge; CeO_2) by a simple electromotoric force measurement series of a galvanic calomel electrode cell of the type

Ag, AgCl	Reference solution (X)	Membrane	Test solution (XX)	Saturated KCl solution	Hg_2Cl_2	Hg

where (X) 0.1 *N* KCl; (XX) 0.01 *N* KCl.

BEHAVIOR OF SPECIAL GLASSES FOR HIGH-VACUUM AND HIGH-FREQUENCY TECHNOLOGY

382. Vacuum-tight *sealings* of glass containers and tubes for modern electronic industry products, prevailingly, require that specifically selected construction materials be used to control the geometric premises for the introduction of metal electrodes into the glass bodies (as insulators) to distribute the axial pressure stresses in metal/glass composites, mostly of the concentrically welded cylindrical units as shown in Fig. 100. D. Fuchs[229] explicitly discussed the thermal expansion conditions for a satisfactory *working* in the range of the softening temperature of the glass which are particularly critical and can only be fulfilled by an accurate

[228] *J. Amer. Ceram. Soc.* **52**, (2), 65–68 (1969).
[229] *Glastech. Ber.* **39**, (3), 149–155 (1966).

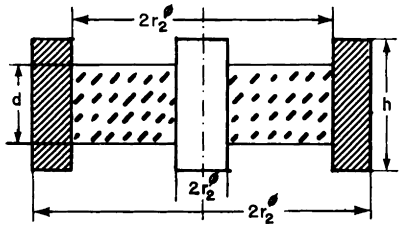


FIG. 100. Principle sketch of a pressure glass bushing. (Fuchs.)

adaptation of the glass to the thermal expansion characteristics of special alloys, mostly of Fe and Ni, with additions of Cr and Mn. Strain-optical interference phenomena may be used to control the pressure stress distribution during cooling after the shaping process of the composites and for a basis of calculation to apply the Adam equation systems[230] in analogy with the uniaxial interference figures (Fig. 101). These strongly resemble the conoscopic patterns known from anisotropic crystals, and are a reliable guide in observing the transition from pressure to tension strains as the so-called inversion temperature T_i indicated during heating up and cooling down of the composites, when the isochromate curves are vanishing. When high-frequency inductive sealing methods are used, temperature gradients which are caused by differences in heat conductivity of the metal and the glass, build up; T_i appears more or less lowered as demonstrated for different Mn or V steel alloys, in combination with the Jena 16 III, or 8421 glasses.

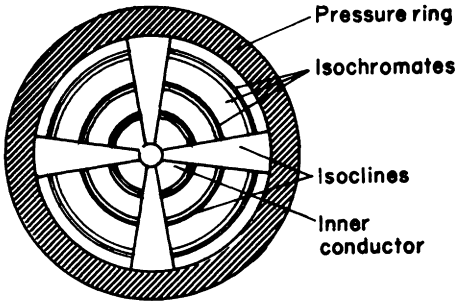


FIG. 101. Schematic representation of the stress-optical interference phenomenon of pressure glass bushing, as observed between crossed Nicols. (Fuchs.)

[230] Cf. H. Adam, *Feinwerktechnik* **58**, (2), 29–40 (1952).

383. PbO-containing glasses play an important role in modern electronics, particularly in the differences between the electric conductance in the massive glass and in surface near layers; structural differences between the inner portions and the glass surface are exaggerated by every kind of heat treatment when alkali ions migrate from the core portion to the surface; cf. H. J. L. Trap.[231] Lead-containing glasses often drastically change their electric conductivity properties when reducing conditions rule on the surface layers and when there are traces of hydrogen in the surrounding atmosphere. These may occur and cause tremendous hindrance in working and also stability problems of high vacuum tube manufacture.

384. Heat-soldered and high-vacuum tight sealings of oxide ceramics (Al_2O_3, or BeO) with metals, and somewhat older techniques of porcelain and forsterite sealings with metals, specifically for electron tubes and rectifier cases, were studied by B. Schmidt,[232] in respect to problems of high thermal expansion coefficients of the ceramic bodies. These may be overcome, however, by sealing onto special alloy conductors like "Nicosil" or "Vacon," using silver–copper alloys as the soldering agents, adding in specific instances gold, tin, Ni, or palladium-coated ceramics with molybdenum, titanium, and manganese oxides, and fluxing agents sprayed in a current of hydrogen and nitrogen at 1250° to 1550°C. For sintering of this kind R. J. Bondley (in 1947) developed the so-called "active metal soldering" techniques which use a suspension of titanium hydride in a high-vacuum furnace (the hydride dissociates at about 650°C in a vacuum of 10^{-5} Torr).

385. High-frequency induction heating for sealing glass onto metal "Nilo K" alloy was described by P. J. Salt.[233] He emphasized that not only the thermal expansion characteristics but also other properties of both the glass and the metal should be investigated to warrant fully satisfactory sealing techniques. The oxidation of the metal, which is indispensable for a strong binding, must be especially carefully controlled to avoid crack formation. Not every kind of crack evolution may be critical for the durability of the products, but in practice it is necessary to classify different crack types in order to detect the imminence of any really detrimental anomalies.

386. Important practical experience combined with valuable recommendations for successful measures to avoid crackings in absolutely high-vacuum-tight sealings of special glasses with metal alloys (of the system Fe – Co – Ni) like Nilo K or Dil P is described in an article by J. P. Davezac.[234] These studies include another interesting

[231] Symp. sur la surf. du verre et ses traitements modernes, Luxembourg, 1967, Compt. rend., Union Scientif. du Verre, Charleroi, 1967, I. 1. pp. 9–27.

[232] *Silikattechnik* **18**, (7), 214–215 (1967).

[233] *Glass Technol.* **8**, (5), 127–130 (1967).

[234] *Verres Refract.* **24**, (4/5), 174–184 (1970).

application of the electron-beam microprobe analytical examination of sealings, and the detection of cracks, recalling representative results previously published by J. P. Hazart and E. Weinryb [235] (cf. ¶ 519).

387. We discussed in Vol. VII. ¶ 273, fundamental studies by M. P. Borom, J. A. Longwell, and J. A. Pask[236] on the electrochemical reactions occurring between iron metal and Co_3O_4-containing glasses of Na disilicate composition, as the groundwork for knowledge of basic *enameling* processes. For glasses containing Co^{2+} ions, the galvanic oxidation potential which is smaller to that for Fe, typical electrochemical reactions take place on the interfaces in which metal dendrites are forming in the glass by reduction, in definite thermodynamic equilibrium conditions. Relatively long distance cation transfer conditions must be considered, principally of the highly mobile Na^+ ions (cf. Vol. VII ¶ 157, 168).

388. Good insulating and thin-film passivation properties are those which make lead aluminoborosilicate glasses particularly valuable and often applied materials in the modern electrical industry. R. C. Buchanan and M. A. Zuegel[237] studied the desirable properties of such glasses over wide ranges of composition, namely the direct current resistivity, the activation energy of conduction over a temperature range from room temperature to about 400°C, and as a function of variations in composition. Particular emphasis was given to the dielectric constant (from 9 to 16). The fundamental properties were chiefly determined by those of the binary partial system $PbO-SiO_2$ which small additions of Al_2O_3 and B_2O_3 strongly modify in the activation energy for conduction by loosening the density.

389. Similar relatively strong effects of only small additions of alumina on the structural and electric properties of low-in-alkali lithium aluminoborosilicate glasses were determined and interpreted by O. V. Mazurin, T. P. Dgebuadze, V. I. Averyanov, G. P. Roskova, and A. S. Totesh.[238] Here, entirely omitting the phase immiscibilities, we mention strong variations in electric conductance and viscosity simultaneously and the dielectric losses (log tan δ) for which K. H. Wagner's theory of highly conducting isolated inclusions, in a matrix (medium) of low conductivity, is fully confirmed and applicable (cf. Fig. 102). It also responds to the influence of different thermal treatments and pronounced maxima of relaxation losses, thus confirming the polar phase present in isolated inclusions.

390. The electric properties and a series of other physical parameters of dif-

[235] *Verre Refract.* **22**, (2), 145–162 (1968).

[236] *J. Amer. Ceram. Soc.* **50**, (2), 61–66 (1967).

[237] *J. Amer. Ceram. Soc.* **51**, (1), 28–32 (1968); cf. VII. ¶ 212–236.

[238] Proc. Conf. Silicate Ind. (SILICONF), 9th, Budapest, 1967, pp. 489–494, Akademiai Kiado, 1968, cf. VII. ¶ 240 ff.

Glass

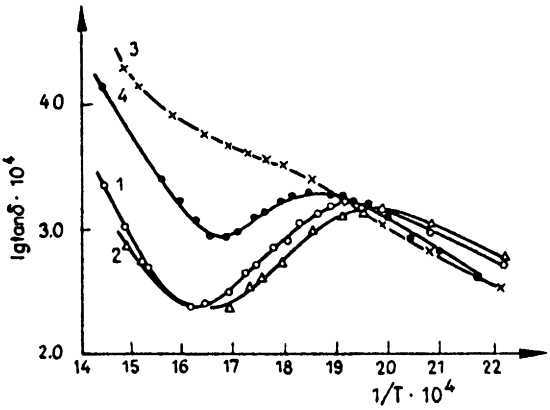


FIG. 102. Total dielectric losses vs. temperature (1) and (2) before, (3) and (4) after, heat treatment at 735°C for 2 hours. (Mazurin, Dgebuadze. Averyanov, Roskova, and Totesh.) Glass composition (1) and (2) $4Li_2O$, $36B_2O_3$, $60SIO_2$; and (4) $4Li_2O$, Al_2O_3, $35B_2O_3$, $60SiO_2$.

ferent glasses containing, besides the normal alkalies and alkaline earths, also B_2O_3, TiO_2, ZrO_2 were examined by V. I. S'hel'yubskiĭ[239] applying a new experimental method which makes possible observation of glass-forming samples in a continuous gradient of concentration in zonal layers, and from point to point, for a rapid classification of glass series, and for a preclassification under practical viewpoints.

391. Electronic surface conductivity of lead silicate glasses and semiconducting glasses as applied in high-sensitivity channel electron multipliers,[240] were measured by H. J. L. Trap[241] in their polarization and ionic distribution on the glass surface and concerning preferential enrichments of certain oxides which reduce the specific surface energy on the migration of metals, heavy metal oxides, or B_2O_3, to the surface, all determined in a potential field of constant 1000 V, under a high vacuum of 10^{-5} Torr, using a mega-ohmmeter (Model Kamphausen, To-7) up to 10^{16} Ω. For a great number of different glasses, the resistance on the surface, κ, and in the bulk glass, ρ, were measured at room temperature and 250°C.

392. The electronic conductivity of Mn, V, and other high-valent elements[242]

[239] Proc. All-Union Sympos. on the Glassy State, 5th, Leningrad, May 25–31, 1969.

[240] Cf. J. Adams and B. W. Manley, *Philips Tech. Rev.* **28**, 156–161 (1967).

[241] *Verres Refract.* **23** (1), 28–37 (1969); for an excellent introduction to this comprehensive publication, see *Sprechsaal* **101**, (24), 1103–1111 (1968); **101**, (24), 1114 (1968).

[242] Cf. H. J. L. Trap and J. M. Stevels, *Phys. Chem. Glasses* **4**, (5), 193–205 (1963).

was determined for lead glasses in a slightly reduced state, namely, $\kappa \times 10^4$ as a function of the square root of time of hydrogen exposure. Above 375°C, agglomeration of the lead takes place and the activation energy of electron transport was anomalously decreased. No electrolysis or polarization effects could be observed; the activation energy for ionic diffusion was about 1 eV, but that for electrons only 0.4 eV. For lead glasses, the thickness of the reduced surface was a few microns, that of the surface nearest layer with electron migration only some 100 Å. Of practical importance is the very particular behavior of Bi_2O_3 (up to 25 mole %) or reoxidation effects of K_2O-PbO silicate glasses during long storage periods. For the Bi_2O_3-containing glasses, the activation energy of electronic conductivity in the reduced surface layer drastically decreases with an increase of the mole percentage Bi_2O_3 concentration, e.g., for 4.0 and 8.4 mole % Bi_2O_3: 0.34 and 0.08 eV, while at the same time, the lead oxide contents diminishes from 10.8 to 2.8%.

COMPOSITES OF SEMICONDUCTOR AND IONIC GLASSES

393. When semiconductor glass films are applied onto a substratum of common glass composition, it is observed very often that the ohmic resistance of the semiconductor material, undergoes in longer time periods, certain anomalous deviations from the initial normal values. According to S. M. Cox[243] resistance may increase by 1–2% after the manufacture of the composite, which is then later followed by a steady decrease. Practical experience in this matter has been collected with tin dioxide resistors, as observed in experiments which included variations in the chemical composition of the substratum glass and of the temperature of the surrounding and in the voltage. These experiments are interpreted to mean that ionic diffusion transfers must have played a definite role by ionic immigration into the glass substratum caused by electric field conditions in the boundary interfaces between glass and semiconductor film which has a metallike nature and thus modifies the semiconductor characteristics in its resistance qualities. The decrease in resistance (after the initial subordinate increase) is doubtlessly caused by the migration mechanism of highly mobile cations in the glass, by elevated temperature conditions, when the dielectric constant of the surrounding medium increases. These factors, combined, cause the evident instability of such resistor composites. Since the decisive contribution to the observed effects are made by ion migration, it is easily understood that in (nominally) "alkali-free" glass, substrates are essentially damped, but in most cases, are not entirely negligible. Typical diagrams of the practically

[243] *Phys. Chem. Glasses* **5**, (6), 161–165 (1964).

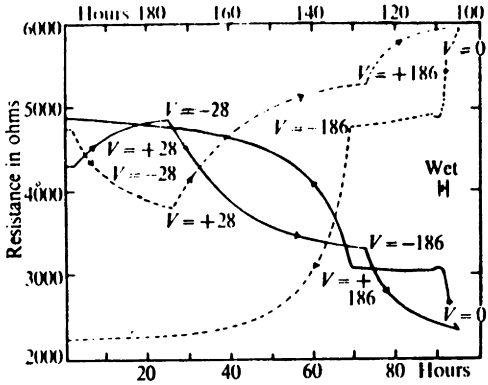


FIG. 103. Resistance variations of oxide films on opposite sides of a soda-lime silicate glass with voltage applied across the glass. The atmosphere was made humid between the tenth and eleventh hours. (Cox.)

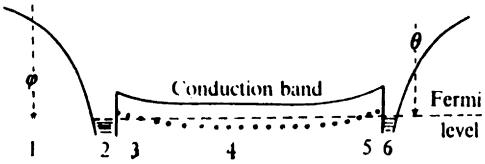


FIG. 104. Electron energy diagram through glass/oxide section: (1) glass, space charge, and ion concentration gradient; (2) interface, ions front glass trapping electrons; (3) oxide, depletion region; (4) oxide; (5) oxide, depletion region; (6) adsorbed surface states. (Cox.)

observed variations in resistance are shown in Fig. 103; Fig. 104 also shows a schematic electron energy diagram for the composite system (i.e., the glass/oxide section).

394. A very peculiar kind of semiconductor glass may be seen according to A. Ishii and K. Aikawa[244] in thallium-stained glasses. After an initial treatment of cation exchange of Tl^+ ions for alkali ions, R^+, in a medium of molten sulfate, ($R = Li^+$, K^+, Tl^+, and Zn^{2+}) and an ensuing reduction of the Tl^+ containing glass in an atmosphere of hydrogen at about 550° to 620°C, the brown-, black-, or gray-stained end product can be shaped in which α- or β-Tl^0 (metal) occurs as a dispersoid phase of particles reaching sizes up to some microns, as a typical "pyrosol" when in the molten form, and as a metal dispersoid glass (type like ruby glass) when solidified.

395. Analogous problems arise when Pb^{2+} is reduced in molten or solidified glasses, or even in crystalling compounds like PbO, Pb_2SiO_4, $PbSiO_3$, $PbTiO_3$, $PbZrO_3$, even in crystalline solutions of the two last-named compounds, when

[244] Asahi Garasu Kenkyu Hakoku **15**, (2), 97–102 (1965).

reduced by hydrogen, as it was studied by G. Haertling and R. L. Cook,[245] with quantitative determinations of the degree to which the corresponding reactions attained—either directly by gravimetric determinations of weight losses, or better by the determination of the dewpoint temperatures of water vapor which was formed by the same reduction reaction. This latter method yields a convenient and reliable way for measurements of the integral amount of water formed according to the simple equation $W_{H_2O} = \rho f \int_{t=0}^{t=t_1} H\, dt$ (H being the humidity in grams of water vapor/grams of the dry carrier gas, ρ the density of the carrier gas at the dewpoint temperature, f the rate of the gas flow). The measurements can easily be made in regular time intervals during every experimental run. The particularly interesting results for reduction of a lead silicate glass are, however, limited by the particle sizes and their surface. Devitrification tendencies are increased by the evolution of surface discontinuities like cracks and crystal grain boundaries in a not easily accurately determined manner. It could be established that below about 300°C, the kinetics of the reactions involved show a first order type, for PbO alone, whereas, for the lead titanate and zirconate, much more complex reaction conditions are indicated. The temperature dependence of the reduction reaction *rates* obey an Arrhenius-type relation.

396. K. Blank[246] measured conductance as a function of temperature and alternating current frequencies for a series of binary and ternary alkali silicate glasses. From the curve for the frequency functions, the so-called direct current conductance could be extrapolated when, with increasing frequency, the conductance increases as a consequence of dielectric relaxation; on the other hand, a decrease in conductance is observed at low frequencies, as a consequence of transition resistivity effects near the electrodes. The alkali ions must evidently overcome a definite potential threshold before entering the glass near the anode, or leave it near the cathode. Under the action of an electric field, alkali-impoverished layers are developing near the anode which are indicated as dielectric loss capacities on the border layers which cause considerable errors in common "direct current" measurements of conductance, e.g., for higher voltages by field strength effects.[247] Applying alternating current of frequencies from 50 upwards to 10^6/second the direct current way conductance can be determined following an experimental law of Arrhenius type: $\kappa = \kappa_0 \exp(-W/RT)$, with an activation energy W for the direct current effect, as a function of the alkali ion concentration. Ternary alkali silicate glasses show, as a rule, considerably higher activation energies than do binary glasses of this class,

[245] *J. Amer. Ceram. Soc.* **48**, (1), 35–40 (1965).
[246] *Glastech. Ber.* **39**, (11), 489–496 (1966).
[247] Cf. J. Vermeer, *Physics* **22**, 1257–1268 (1956).

and their parameter κ is considerably larger than is that for binary ones, this to be explained by a higher functional dependence of the activation energy for ternary glass systems on temperature (cf. O. L. Anderson and D. A. Stuart).[248]

397. The production of very thin, optically efficient layers on glass surfaces were fundamentally studied by H. Schröder[249] in their applicability to large variation areas. Whereas, for such purposes, the vapor condensation method *in vacuo* is specifically advantageous, for the deposition of metals (only in single cases, they are deposited by reduction from metal salt solutions onto the glass) dielectrics or semiconductor layers may be applied to a glass substratum by dipping with the ensuing decomposition of easily destroyable metal compounds, and by cation exchange and diffusion. All such methods are advantageously introduced in the manufacturing of selectively reflecting or absorbing coatings, and for the reduction of surface reflection by an application of nyonreflecting films ("Entspiegelung" in German practice) of plate glass. For special examples for such different technological methods, cf. ¶ 285 f., and on glasses with selective reflection properties see Ref. 250. Specifically interesting are experiments made with a directed change in the reflection in the infrared range to reduce the heat energy input, by absorption in the visible spectral ranges, and in the ultraviolet range by reducing the radiation and reflectance. The vacuum vapor condensation of gold onto sheet glass to make optical glass, is economically possible for large areas only when the layer thickness of the deposits is minimal.[251] The best technological method recommended by Shröder is still the precipitation of metals from organometallic solutions. Combinations of such layers in superposition, open possibilities for an adaptation to more specialized requirements in the coating effects.

398. In the systems $Ag_2O-P_2O_5-MoO_3$ and $K_2O-P_2O_5-MoO_3$, J. D. Provance and D. C. Wood[252] investigated the glass-formation range by X-ray diffraction analysis and by studying the temperature coefficients of the electric resistivity and linear expansion in correlation to technological properties, like the durability and density, and the extinction of compositions with semiconduction characteristics[253] (cf. Vol. VII. ¶ 206, and J. D. MacKenzie).[254] Electronic conduction

[248] *J. Amer. Ceram. Soc.* **37**, 573–580 (1954).

[249] *Glastechn. Ber.* **39**, (3), 156–163 (1965).

[250] See also *Glas Email Keramo Tech.* **17**, (5), 161–165 (1966), and extensive experimental studies of H. Schröder *Verre Réfract.* **18**, (2), 89–97 (1964).

[251] On vacuum metallization of ceramics *in vacuo* by gas discharge see D. M. Mattox, *Bull. Amer. Ceram. Soc.* **43**, (8), 586 (1964); *J. Amer. Ceram. Soc.* **48**, (7), 385–386 (1965).

[252] *J. Amer. Ceram. Soc.* **50**, (10), 516–520 (1967).

[253] Cf. F. Seitz, 1940; Bh. Janakirama Rao, *J. Amer. Ceram. Soc.* **48**, 311–319 (1965).

[254] *J. Amer. Ceram. Soc.* **47**, (5), 211–214 (1964).

is dominant, polarization effects are only subordinate, inhibiting ionic conductivity by a more stable structure as a result of the Ag^+ ions in the glass. A double (electronic-ionic) mechanism of conduction is presumed in view of distinctly increasing resistivities with time.

399. For investigations of iridescent layers of titanium and tin dioxide on glass surfaces, E. W. Wartenberg and P. W. Ackermann[255] started with ancient luster techniques (applied in the Tiffany Favrille manufactures) by spraying metal chlorides with water, inducing a rapid hydrolysis, combined with typical "hardening" effects of the glasses. Solutions of $SnCl_4$ in benzene are recommended as spraying systems; chlorobenzene or trichloroethylene are recommended as spraying systems to deliver the tin dioxide by reaction with water vapor at temperatures of between 400° and 740°C. The thickness of the SnO_2 layers deposited may be about 10^3 Å. They are typical *n*-type semiconductors. For the three organic solvents mentioned above, the speed of oxide film formation does *not* depend on their chemical nature; with CCl_4 and C_4H_9OH anomalies occur. The temperature of the substrate exerts an important influence on the electric characteristics of the oxide layers. In their X-ray diffraction the SnO_2 layers show fully crystalline cassiterite structures, and crystallographic orientation effects may also occur. Layers produced in CCl_4 and C_4H_9OH solutions as solvents show a surprisingly high resistance which evidently is caused by multiple fissuring of the oxide layer surface; the addition of only 1% methyl alcohol markedly reduces this undesirable effect.

400. Glass tubes of a high-percent PbO content show, after J. I. Genco and B. C. Almaula,[256] that reduction in a hydrogen atmosphere may occur with a maximum surface conductivity for one optimum reduction temperature (400° to 430°C), whereas the increase in conduction after a reduction period of more than 7 hours is insignificant. The minimum of resistance is at $7 \times 10^{13}\ \Omega/cm^2$. In spite of the doubtlessly strong rugosity of the surface of the reduced glass, as observed by electron microscopy, there is no clear correlation between conductivity and rugosity, but there are effects of a chemical pretreatment on the surface conductance and the intensity of reduction of PbO to Pb metal by CO in the surrounding atmosphere.

401. On the influence of high electrostatic field potentials in their effects on glass conductivity (examined were common Na–Ca silicate and Na borosilicates, up to 9500 V) and the deviations from Ohm's law, see L. Žagar and E. Papanikolau[257] using reversible electrodes ($E = 5 \times 10^5$ V/cm), when a critical field intensity is excelled, above which the H. H. Poole (1916, 1921) theories should be applied. Most

[255] *Glastech. Ber.* **41**, (2), 55–62 (1968).
[256] *Bull. Amer. Ceram. Soc.* **48**, (9), 848–849 (1969).
[257] *Glastech. Ber.* **42**. (2), 37–44 (1969).

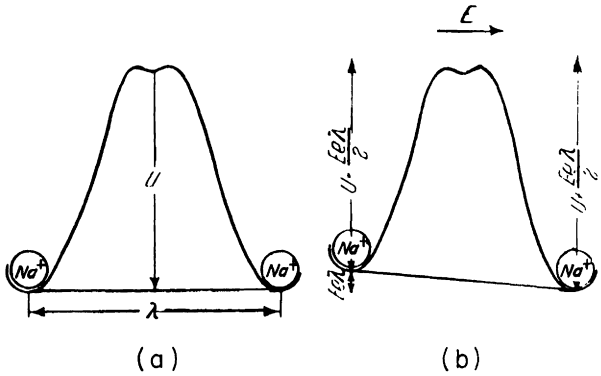


FIG. 105. Definition of the jump distance. (Cf. ¶401 for details) (Žagar and Papanikolau.)

unexpected may be that jump distances, λ, of the charge carriers, e.g. Na^+ ions are rather independent of the temperature, and also of the chemical composition of the glass. A jump distance of 48 Å corresponds to an average distance of $Na^+ - Na^+$ ions very closely (Fig. 105a). Figure 105b shows for the electric field E an asymmetry in the potential "hill", thus creating a modification of the activation energy U in the direction of the field by the amount of $-\frac{1}{2}Ee\lambda$, in the counter direction of $+\frac{1}{2}Ee\lambda$.

402. A glass of somewhat unusual composition in the ternary system $ZnO-B_2O_3-PbF_2$ was developed by T. Hikono, M. Mikoda, and S. Hayakawa,[258] and was technologically introduced with considerably improved properties into practical electronics techniques. The properties of adhesion to metals, the thermal expansion coefficient, and water solubility depend very much on changes in the chemical composition of such glasses.

403. That even slight degrees of reduction of lead silicate glasses with the formation of metallic lead are very sensitively indicated by intense staining phenomena is generally known. It was described anew by W. Hupper[259] during fusion of such a glass in a low- or medium-frequency (50 to 15,000 Hz) alternating current field when the well-known but undesirable "metal fogs" developed, especially for the walls of platinum crucibles. Spectrophotometric measurements over the range of $\lambda = 350$ to 600 mμ show strong absorption bands for the dark-stained glass. Concerning the influence of current density versus frequency ratios, a distinctly critical value exists where the precipitation of lead stops, corresponding to a charge density

[258] *Nat. Tech. Rep. Matsuhita Elec. Corp., Osaka* **14**, (1), 67–70 (1968).
[259] *Silikattechnik* **22**, (3), 389–393 (1971).

of 2.5×10^{-3} a/cm^2 for a fusion temperature of 1100°C. An increasing content of silica in the glasses induces the precipitation of the lead; when alkalies replace silica in the glass composition, the extinction data increase. The lead precipitation from the melts is symbatic to the atomization of platinum from the electrodes.

GLASS–METAL SEALING PROBLEMS

404. Soldering glasses which nowadays are widely applicable in electronic equipment manufacturing, were studied in the simple ternary composition system $PbO-ZnO-B_2O_3$, by J. Broukal.[260] Such glasses must be melted in a strongly oxidizing atmosphere in alumina crucibles. In the center of such investigations was the determination of the coefficients of thermal expansion, the dilatometric deformation temperature M_g (cf. Vol. II.A. ¶ 26, 88), and the transformation point temperature T_g. The contact angle of the glass melt with the surface of the metal substratum is of direct importance for the application of one or the other of the disposable soldering glass compositions. New aspects are opened when crystallization of Pyroceram-like "glass-ceramics" are inserted into the soldering process proper because it brings about considerably improved mechanical properties in comparison with those brought by the commonly used methods, and it guarantees an excellent vacuum tightness of the soldered material composite. For lead–zinc borate solder glasses, the softening intervals are 300° to 400°C, the temperatures of crystallization about 485°C, indicated as peaks on the differential-thermal analysis curves. The devitrified material softens at higher temperatures than the original glass, namely at 490° to 500°C.

405. Glass/metal sealings, in their thermal expansion characteristics and their behavior in the transformation range, were studied by L. F. Oldfield,[261] first for an interpretation of certain anomalies occurring in the application on molybdenum and wolframium. It must be emphasized that for a control of a successful sealing process, it is not sufficient to measure only the thermal expansion from room temperature up to 350° or 400°C; even glasses of one and the same chemical composition may show differing behavior in the sealing range which easily may cause serious stress and strains in the glass/metal bonds. Slightest changes in the content of B_2O_3 may be responsible for highly undesirable irregularities in the critical temperature range between 400° and 430°C on cooling with variable rates. For the sealing of Mo glass, some improvement may be possible by a prolonged thermal exposure at 380 to 450°C over 100–140 hours. Equal phenomena are discussed by Oldfield for a sealing of

[260] *Silikattechnik* **13**, 428–433 (1962).
[261] *Glass Technol.* **5**, (4), 150–156 (1964).

glass/Wo. It may occur that for glasses alleged to be of identical chemical composition and with the same thermal expansion coefficient between 20° and 350°C in the interval between the deformation and the transformation points, a rather different expansion rules. There is even no clear correlation between the contraction differences and the actual stress and strains in the sealings at room temperature because of delayed elastic relaxation effects, and differences in the rates ruling these mechanisms in the critical range of a viscosity of about 10^{14} P, the so-called "setting points." These highly complex phenomena are illustrated in a three-dimensional schematic diagram over the temperature range from room temperature to 560°C by the differences in deformation and stress effects of an anomalous relaxation (Fig. 106).

406. In a second publication concerning the problems of borosilicate sealing glasses with different metals[262] Oldfield gives a comparative presentation from ex-

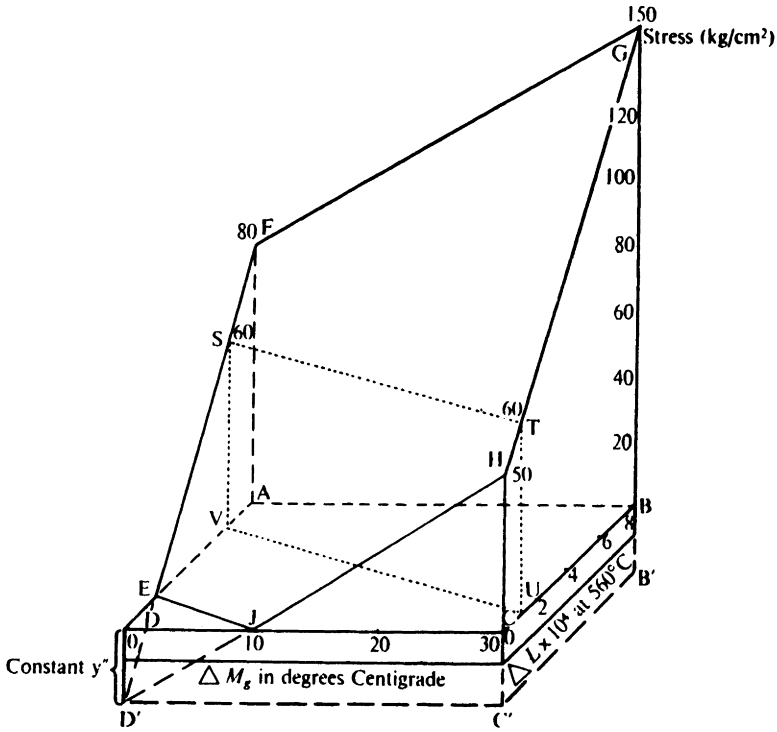


FIG. 106. Solid model for the dependence of the mean interfacial stress on differences in the M_g points and specific elongations for pairs of tungsten sealing glasses. (Oldfield.)

[262] *Glass Technol.* **5**, (6), 224–229 (1964).

perience with reexpansion properties of 33 different glasses for sealing with Mo, Wo, and Fe–Ni–Co (Nilo K) alloys, their T_g and M_g point temperatures, and the important intervals between these fix points in correlation with the thermal expansion characteristics up to 500°C, elongations from room temperature to T_g and M_g (the dilatometrically determined deformation), and between T_g and M_g proper, with a wealth of numerical data. Concerning the chemical factors ruling those correlations, we may emphasize a nearly linear correlation of M_g with increasing silica concentration, whereas for T_g, two distinctly different, but nearly parallel trend lines are derived. When T is plotted as a function of the ratio SiO_2/B_2O_3, low values of this ratio correspond to low values of T_g. Typically anomalous, however, is the behavior of Li-containing glasses, and those with about 5% BaO.

407. About this eminently important field of glass technology applied to electronic instrumentation tasks, we may also include observations made by T. Takamori and M. Tomozawa[263] concerning glass interlayering glass/Wo sealings. Their composition can be controlled by X-ray diffraction analysis of the layers in different degrees of staining intensity, namely, WoO_3, $Wo_{18}O_{49}$, and "alkali–Wo bronzes." For the mechanical strengths of the sealing effects even small differences in the thermal expansion of those different substances are essential. Wo bronzes are absent in glasses without alkalies; for this reason, layers of glass/Wo have greater mechanical durability than the common alkali-containing sealing glasses. The observation of changes in the color tints of such interlayers of sealed specimen after controlled heat treatments may be very useful in any survey of the qualities of sealed products.[264]

408. We owe to J. A. Pask and M. P. Borom[265] an oustanding monograph on the problems involved with chemical equilibrium of glass/metal sealings in the presence of oxygen between the molten glass and the metal. This complex problem is typical of reactions taking place on phase boundaries, and their kinetics. The basic idea of the authors is that continuous and coherent electronic structure and chemical bonding is only possible when a state of equilibrium is established, the problems of adhesion here included, as postulated by equilibrium postulates of boundary surface energies (cf. ¶ 353, 368). That the wetting angle would tend to the zero value is compatible with a building up of rigid chemical bonds as the principal condition required for satisfactory adhesion (cf. Vol. II.A. ¶ 392 ff., 409).

[263] *J. Amer. Ceram. Soc.* **48**, (8), 405–409 (1965).

[264] See among other special literature the studies made by M. E. Straumanis, *J. Amer. Chem. Soc.* **71**, (2), 674–683 (1949) on Wo bronzes.

[265] Rep. UCRL—118 16 Rev. AEC Contract No. W-7405-eng-48; Univ. of Calif., Berkeley, Lawrence Radiation Lab., No. 33, 1965.

409. Another excellent series of eminently important practical experience and recommendations on the sealing of *glass-ceramics* with metals (and alloys) was presented by P. W. M. McMillan, B. P. Hodgson, and G. P. Partridge.[266] The first step is application of the glass melt onto the metal and the second, the crystallization of this glass to the "Pyroceram"-type glass-ceramics body, with all its well-known, valuable physical properties, excelling those of the common glass, and combining these to achieve the highest possible impact and dielectric strengths. Chemical reaction of the glass-ceramic substance during sealing onto the metal surface can be avoided by introducing small amounts of P_2O_5 into the glass composition and the nucleating agent. The commonly used TiO_2 nucleator must be excluded because of its easy reductibility and its semiconductor character in the partially reduced state. A particularly applicable composition of the glass-ceramics is from the system $Li_2O-ZnO-SiO_2$ with slight additions of P_2O_5 and alkalies, the crystallization temperature being 700° and 900°C. A second publication by the same authors[267] offers many details for the application of intermediate bonds (fillets) of different glass melts with metal solders like Armco iron or copper. A slight preoxidation of the metal in an atmosphere of 90/10 nitrogen/argon is furthermore recommended; solders on the basis of Ag–Cu, with additions of Ti or Cu, for soldering *in vacuo*, or argon also are recommended.

410. Preparing sealing glasses on the basis of low-melting systems like $PbO-ZnO-B_2O_3$ or $PbO-Bi_2O_3-B_2O_3$, for package (encapsulation) of silicon semiconductor devices was described by M. Ishiyama, T. Matsuda, Sh. Nagahara, and Y. Suzuki[268] for sealing temperatures of less than 375°C at which the glass powder surface begins melting and a smooth surface of glass appears. To keep the fusion temperatures low, additions of Bi_2O_3, CuO, TiO_2, and PbF_2 were successfully introduced to improve the fluidity and durability in contact with water, and to keep volatilization of Pb as low as possible. In this connection, we may mention an interesting, detailed investigation of the system $PbO-ZnO-B_2O_3$, by J. Petzold[269] which shows in its phase diagram (cf. ¶ 404 and Fig. 107) a surprisingly complex multiplicity of binary and ternary compounds in fields of coexistence of which those for $2PbO \cdot ZnO \cdot B_2O_3$, $PbO \cdot 2ZnO \cdot 3B_2O_3$, and $4PbO \cdot 2ZnO \cdot 5B_2O_3$ are important and can be identified by mineralogical microscopic methods and X-ray diffraction analysis data.

411. For practical purposes, the results of a symposium on methods for the

[266] *Glass Technol.* **7**, (4), 122–127 (1966).

[267] With H. R. Heap, *Glass Technol.* **7**, (4), 128–133 (1966).

[268] *Asahi Garasu Kenkyu Hokoku* **16**, (2), 77–88 (1966).

[269] *Glastech. Ber.* **39**, (3), 130–136 (1966); cf. the older investigations by A. E. Dale and J. E. Stanworth, *J. Soc. Glass Technol.* **32**, 147–153 (1948).

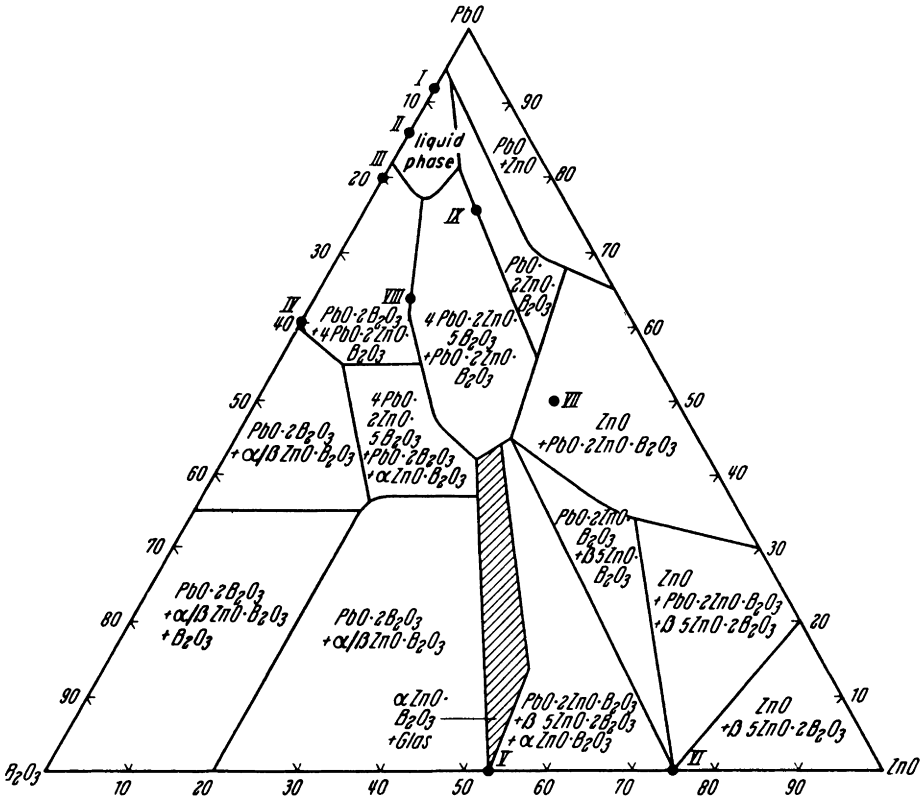


FIG. 107. Coexistence regions of different phases in the ternary system $PbO-ZnO-B_2O_3$. (Petzold.)

measurement of thermal expansion parameters of solder glasses and their relation to those of metals with which they are to be soldered, are discussed by A. S. Totesh,[270] concerning the prerequisites of the glasses for satisfactory bonding effects. Coming back to the aforementioned article by J. Broukal (see ¶ 404) on the devitrification of solder glasses, he has another publication[271] on the system $PbO-ZnO-B_2O_3$ with the highest, $PbO-B_2O_3-SiO_2$ with the lowest, coefficients of thermal expansion. For positive results in attempts to develop glass-ceramics from such compositions which might be useful as solder glasses (e.g., at 450°C determined for color television tubes), a viscosity in the soldering operation of about 10^4 to 10^6 P is optimum. One difficulty is that the crystallizing glasses show a tendency to wet the

[270] *Steklo Keram.* **23**, (7/8), 398 (1966), (Engl. transl.).

[271] *Silikattechnik* **17**, (8), 242–248 (1966); with many valuable diagrams.

supporting metal less well by far than do common stable glasses, e.g., Kovar alloy. Crystallization of α- and β-$ZnO \cdot B_2O_3$ could be identified by X-ray diffraction analysis in the devitrification products of solder glasses of a texture (with individual crystals of 6-μ size) much coarser grained than is the rule in Pyroceram, for an example. In general, Broukal worked only with the compositions of the systems $PbO-ZnO-B_2O_3$ and $ZnO-B_2O_3-SiO_2$, with slight additions of Al_2O_3, V_2O_5, BaO, CdO, and Li_2O; the latter exerts rather strong modifying effects.

412. For the encapsulation of semiconductor monocrystals (of Si) D. W. A. Forbes[272] described special solder glasses for sealing which are adequate when they are transferred by a thermal aftertreatment to glass-ceramics of improved technological qualities, particularly of increased durability under stress–strains caused by the sealing operation itself. Forbes recollects the artifice of adding lead–zinc borate *frits* containing a crystallization nucleator substance or "fillers" introduced by admixture. The favorable effects could be observed and demonstrated by electron microscopy of the crystalline structures shown in casings for semiconductor schedule writings to be shaped in *one* operation together with the shaping of the casing, i.e., finally with the sealing of the cap. The differential-thermal diagram for a lead–zinc borate glass, together with the curve for the thermal expansion, is seen in Fig. 108. Concerning the *adhesion* of difficultly sealable layers of molybdenum on alumina (corundum) ceramics, see also H. Rochow[273] (cf. Vol. II.B. ¶ 151).

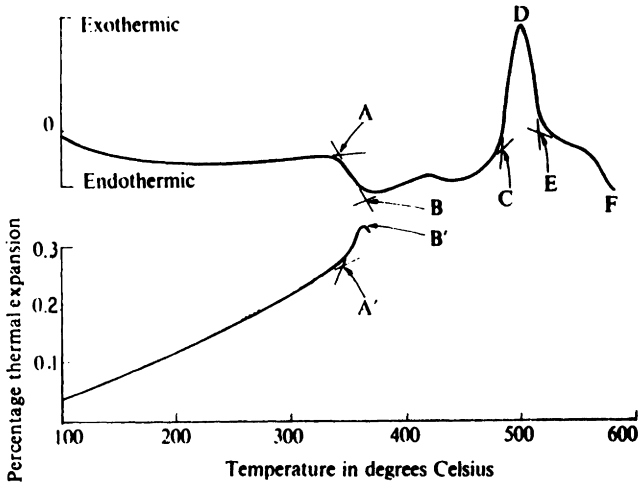


FIG. 108. Differential-thermal analysis curve (thermogram) of a solder glass in the ternary system $PbO-ZnO-B_2O_3$, and the corresponding curve of thermal expansion for comparison. (Forbes.)

[272] *Glass Technol.* **8**, (2), 32–42 (1967).

[273] *Ber. Deut. Keram. Ges.* **44**, (5), 224–231 (1967).

413. The supremacy of glass-ceramic-type soldering processes over the usual simple glass-soldering methods becomes highly evident in another publication of W. Sack, H. Scheidler, and J. Petzold,[274] chiefly by a notable improvement of the thermal expansion behavior during soldering. Crystallization (devitrification) of solder glasses is best controlled when the glass applied is a rather fine powder (with particles of 60 μ in diameter) and can be best surveyed by differential-thermal analysis, as a reliable and rapid laboratory method in combination with a control of the crystallization rate using the Ponomarev–Grauer–Hamilton temperature gradient method (cf. Vol. II.B. ¶ 138, 210). In typical solder glasses, the maximum rate of crystallization is not more than 2.0 μ/minute with a scattering far lower than that usually observed with common and optical glasses. In this respect, the behavior of solder glasses is comparable to that of glass compositions for real Pyrocerams.

414. The crystallization behavior of $PbO-TiO_2-B_2O_3$ glasses was examined by Y. Suzuki and N. Ichimura.[275] These glasses have such a high tendency to devitrify that they can be obtained only by a rapid quenching in a water-cooled rolling machine that forms thin films. The differential-thermal analysis characteristics of these interesting glasses were studied as a function of slight changes in the chemical composition among which the most interesting decreased in the linear expansion coefficients with an increasing content of TiO_2 introduced as precipitated lead titanate, $PbTiO_3$, of perovskite type, which has a strong negative value for this coefficient. Nevertheless, it was found that the expansion coefficient of the crystallization products is not quite as low as could be expected. The practical evolution of electronic construction elements in which glasses and glass-ceramics soldered onto metals are required, is outlined from the newest viewpoints of engineering in a very instructive article by O. Vinz,[276] particularly in view of the very narrow tolerance which is permitted in the production of semiconductor diode casings which require a very short thermal exposure of the silicon monocrystal, and a very constant and exactly controlled axial contact pressure. This latter problem could be solved by adequate radiation heating in the place of flame heating for the closing of the casings. For these enormously critical requirements, the introduction of a very thin circumferential shielding layer of a black enamel was particularly successful.

415. New methods of electronic devices require, for real micro miniaturization and high packing density, the introduction of a critically small (local) infrared radiation heating of the glass elements which must contain for a safe function, infrared-absorbing "doping" ingredients among which Cu is proposed to replace the

[274] *Glastech. Ber.* **41**, (4), 138–145 (1968).
[275] *Asahi Garasu Kenkyu Hokoku* **18**, (2), 49–58 (1968).
[276] *Sprechsaal* **101**, (15), 623–628 (1968).

commonly used Fe, with a high PbO content, which melts rapidly in an oxidizing atmosphere. Necessary adjustments of the thermal expansion coefficient to the transformation points of such Cu radiation glass compositions are critical, again, and the subject of a more recent publication by H. Hoogendoorn and Br. Sunners,[277] which concerns materials of high thermal gradients and thermal shock resistance. The absorption of such a Cu-containing glass must be empirically adapted to the emissivity of the parts to be sealed; Fig. 109 shows a few curves of Cu-doped glasses for an infrared absorption from 0.8 to 1.0 μ, and a Cu content from 0.1 to 5.0%, for an accurate control of the correct heating schedules of the sealing glass to be applied onto the metal.

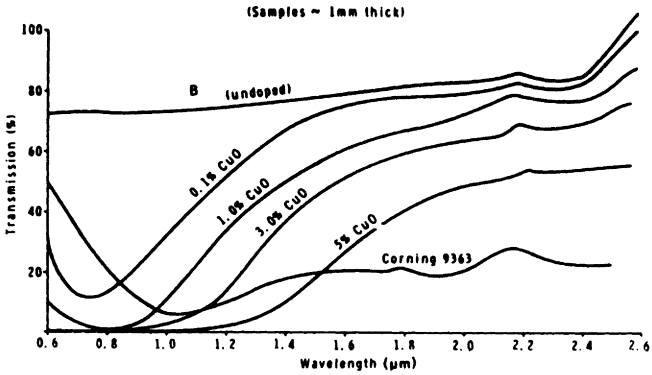


FIG. 109. Infrared transmission curve of a lead aluminoborosilicate glass doped with copper oxide in concentrations from 0.15 to 5 wt. %. (Hoogendoorn and Sunners.)

[277] *Bull. Amer. Ceram. Soc.* **48**, (12), 1125–1127 (1969).

Chapter V

Chemical Durability of Glass

INTRODUCTION

416. The tremendous importance of every chemical reaction occurring between glass and water or aqueous salt solutions is most evident; proper attention must be given to the theories and experimental results of glass hydrolysis for application of most elaborate methods and standard examination principles for all kinds of technologies which use glass, either for simple containers, for pharmaceutical medical purposes, or optical glass, all with precise and responsible requirements in these extensive fields, for which there is a rich literature, special information, and strict specifications. We must restrict our text to some of the most important problems and facts.

417. We start from highly instructive studies made by M. A. Rana and R. A. Douglas,[1] on the reaction of glass with water, in general, and with emphasis on critical viewpoints as derived from experimental methods and observations made in extensive laboratory practice with simple Na–Ca silicate glasses as examined for leachability in a Soxhlet-type apparatus, either with distilled water over a temperature range up to 100°C or under elevated pressures in autoclaves. The well-known law that extraction amounts are proportional to the square root of the time of examination, is ideally fulfilled only in the early periods of leaching and followed by a continuous rate of the extraction reactions. The well-known improvement of chemical durability by introduction of CaO into the glass composition is of equal fundamental significance.

418. A continuation of the studies by Rana and Douglas[2] gives a thorough discussion of the experimental results focusing the importance of the diffusion coefficients for the alkali ions Na^+ and K^+, as a function of glass composition and the activation

[1] *Phys. Chem. Glasses* **2**, (6), 179–195 (1961), with a wealth of numerical data, graphs, and literature references, including experimental equipment details.

[2] *Phys. Chem. Glasses* **2**, (6), 196–205 (1961).

energy of the reactions of glass with water. It is emphasized that the correlation to the A. Einstein equation for the electric conductivity is only a bit satisfactory. The authors are, however, of the opinion that a simultaneous leaching of silica from the glass is the origin of the different anomalies. There is also no convincing correlation of the results to an assumption of a concentration-dependent diffusion regularity.

419. E. Wiegel[3] reported on hot-leaching experiments with highly diluted acid solutions, e.g., pH = 5.8, for different Na–Ca silicate, and borosilicate glasses of the conventional hydrolytic classes (conforming to standard DIN 12 111 for grit extraction testing). Neutrality conditions were included in the investigation program as well as the improvement effects (increased water durability) after surface treatments with slightly acid solutions. Finally autoclave (low-pressure) tests (at 120°C), corresponding to the requirements specified for the examination of pharmaceutic container glass were also excluded. A critical discussion is presented of the manner in which such mild autoclave tests may be too favorable or even directly misleading (cf. E. Wiegel[4]). In the same way, Wiegel[5] studied the hot-leaching effects of neutral salt solutions on silicate glasses, including the very pure Na–Ca silicate MacInnes glass for glass electrodes and borosilicate glasses of the best hydrolytic classes (I to II). The general result of these investigations was to establish a general rule that the standard classifications are not strictly valid in glass testing with neutral solutions, and that, e.g., the amount of bases extracted by solutions of potassium chloride, is distinctly higher than that extracted by those of sodium chloride. On the other hand, results obtained with the glass grit extraction method, e.g., with container glass at 100°C, were confirmed by parallel tests using the surface-leaching principle.

420. E. Wiegel[6] extended his studies with neutral salt solutions to variations in temperature and pH, using the standard grit test with bottle glass (hydrolytic classes III to V) and special medical glasses for infusion flasks and syringes. As a typical "salt effect," Wiegel attributed the pronounced minimum of hot extraction at 0.01 mole solutions, and a maximum for 0.1 mole. Considerably higher leaching effects were observed in the salt solutions, relative to pure distilled water at 100° and down to 25°C ("salt sensitivity" of certain glasses). Surprisingly, Na–Ca silicate glasses for containers, when exposed to leaching with dilute acid solutions, deliver considerably *lower* base amounts than pure water does, and at pH = 3 to 4, the typical improvement effect is observed (e.g., a 40% PbO-containing glass for prisms).

421. Problems of testing industrial and optical glass on their resistivity to *weather-*

[3] *Glastech. Ber.* **38**, (4), 166–171 (1965).

[4] *Wiss. Abh. Tech. Bundesamt, Braunschweig* **15**, 26(1963). *cf.* D. A. Mac Innes, and M. Dole *Ind. Eng. Chem. Anol. Edtn.* **1**, (1929), p. 57.

[5] *Glastech. Ber.* **37**, (3), 141–147 (1964).

[6] *Glastech. Ber.* **42**, (7), 277–284 (1969).

ing were discussed by H. Wessel,[7] from the viewpoints of lengthy observation (for the beforementioned prism glass, over a 30-year period of service), as a purely hydrolytic reaction under special control of "dimming" and straining (spotability) phenomena, commonly called a "haze."

422. The physical-chemical reactions taking place in the hydrolytic extraction of Na–Ca silicate glasses were analyzed by L. Žagar and K. H. Horina[8] for the conditions given in the commonly used Soxhlet method using glass grit of particle sizes from 0.2 to 0.3 mm in diameter.[9] An analytical determination of the extraction products combined with measurements of the electrolytic conductivity for the temperature range from 80° to 150°C indicate that in the first stages of the leaching process the migration of Na^+ ions is the most striking effect, probably together with some migration of Ca^{2+} cations from the glass into the solution. This migration increases, but after a longer period, the glass surface is eroded, particularly when the temperature is increased. With an increasing Na_2O contents of the glass substance, the rate of the Na^+ diffusion increases, but it is again reduced when increasing amounts of silica go into solution. The diffusion coefficients were controlled continuously in correlation with the electric conductivity. Those coefficients, when directly measured, are considerably lower than those calculated from the leachability. Nevertheless, an essentially better agreement between both groups of coefficients can be found when one may introduce into the Nernst–Einstein equation $\mu/D = q/kT$ (μ the ion mobility, D the diffusion coefficient, q the electrostatic ion charge), not the electrolytically determined Na concentration, but the "electrolytical concentration," the number of current-transferring Na^+ ions, i.e., the value $Z = h\kappa_\infty/e^2\lambda^2$ (λ being the jump distance of the Na^+ ions, cf. ¶ 401, and Eyring's theory of rate processes).

423. L. Žagar and G. Krause[10] determined from well-defined glass powders the grain-size fractions over the range from 37.7 to 60.3 μ—using the semiautomatic Endter and the electronic Coulter counter (cf. Vol. VI.C. ¶ 51). For the determination of the specific surface, they used the gravimetric nitrogen adsorption (BET) method; special care was given to typical aging effects of the glass surface, as a function of time, and under definite curing conditions. The glass grains were in no way isometric in their shapes, but somewhat elongated (ratio length/diameter = 1.13:1), the average grain-shape factor = 17.15. When the glass samples were cured in a moist atmosphere the specific surface is gradually increasing, the more rapidly the higher the alkali concentration in the glass, by the evolution of hydrogel films on the glass surface.

[7] *Silikattechnik* **14**, (4), 112–119 (1963).
[8] *Glastech. Ber.* **37**, (5), 235–245 (1964).
[9] Cf. Žagar and A. Schillmöller, *Glastech. Ber.* **33**, (4), 109–116 (1960), cf. II. B. ¶ 166.
[10] *Glastech. Ber.* **39**, (4), 177–186 (1966).

424. L. Žagar, H. Lüneberg, and G. Boymanns[11] gave a detailed description of a modified Soxhlet extraction instrument which was used for leachability tests of strontium silicate glasses in which the flow rate of the leaching liquid solution through the glass powder bed could be controlled. For this purpose, the leaching cell was furnished with exchangeable nozzles of different apertures which made possible a variation of the flow rate periods from 5 to 50 ml/minute. The concentration of the leachates in this modified cell device was found distinctly smaller than that previously observed in experiments with a stagnant solution liquid. Flame-photometric control of the Sr^{2+} ions in the leachates agree best with the equation $Q = At^n$ (Q being the leached material amount as a function of time t; n being = 0.30 to 1.20; 0.50 would correspond to the value for pure diffusion). The ratio Si/Sr in the special strontium glass studied is independent of time; the Sr extraction proved to be more rapid than the destruction of the Si—O skeleton in the framework of the glass.

425. The preparation of samples for chemical durability tests which was so carefully studied by Žagar and Krause (see above) was also studied by R. F. K. Sykes,[12] who found that the alkali losses from thick-walled tumbler samples (6 mm) were 5–8% larger than those from thinner walled samples (1.5 mm), when the grit extraction method was applied in combination with titrimetric and flame-photometric determinations of the leachates. This fact was tentatively explained by the formation during crushing of compacted agglomerates which do not disintegrate during rinsing and the chemical leaching test, although they have a much larger leaching surface and, therefore, send out about 50% more alkalies than the homogeneous glass grains of apparently the same size. This illustrates the necessity of destroying the agglomerates before leaching, by intense friction applied under cover of water-free ethyl ether.

426. S. Ramachandran[13] determined the chemical durability of industrial glasses by analytical determinations, chiefly of Na_2O, SiO_2, B_2O_3. A new confirmation of the $\sqrt{t}$ law for the amounts of extracted material was established in parallel with previous observations of M. A. Rana and R. W. Douglas (cf. ¶ 417 ff.).

427. For *estimating* the surface area of glass grit material prepared for leaching, P. A. Sewell[14] made valuable observations on the application of the BET (nitrogen adsorption method at the temperature of liquid nitrogen), but in a modification on the basis of gas-chromatographic measurements in which the figurative surface area of grits (after sieving and repeated rinsing and scouring) could be directly used as the bed. The results may show more or less systematically strewing data, due to mutual adhesion of the finest particles on the grit grains, an agglomeration of the

[11] *Glastech. Ber.* **42**, (3), 81–83 (1969).
[12] *Glass Technol.* **6**, (6), 178–183 (1965).
[13] *Bull. Centr. Glass Ceram. Res. Inst. (Calcutta)* **12**, (4), 17–22 (1965).
[14] *Glass Technol.* **10**, (1), 9–14 (1969).

finest powder substance, or to inherent irregularities in distribution of the basic surface areas of the grits. The role of agglomerates is chiefly significant because they rule the real surface areas as given in measured data. Under normal well-chosen assumptions, one may learn that in the majority of the data from gas-chromatographic methods the surface areas fall within the shaded region of the diagram, the slope evidently being in a reasonable agreement with Sykes' extraction data for similar grit sizes (see ¶ 425 above). Figure 110 makes it evident that the surface of the grains increases as the numbers of agglomerations increase in the sample, although in a not easily derivable correlation.

428. The important question of whether the surface reactions of pure molten Na and K hydroxide on Na–calcium silicate or borosilicate, or aluminosilicate and zircon silicate glasses at temperatures of 350° and 450°C, respectively, can be compared with hydrolytic leaching effects, and for molten alkali salts, was examined by investigations of R. F. Bartholomew and T. R. Kozlowski.[15] Analogies among those reactions may no doubt exist; speak of a certain "chemical durability" effect on the basis of acid–base concepts in which the glass framework of the reagent would

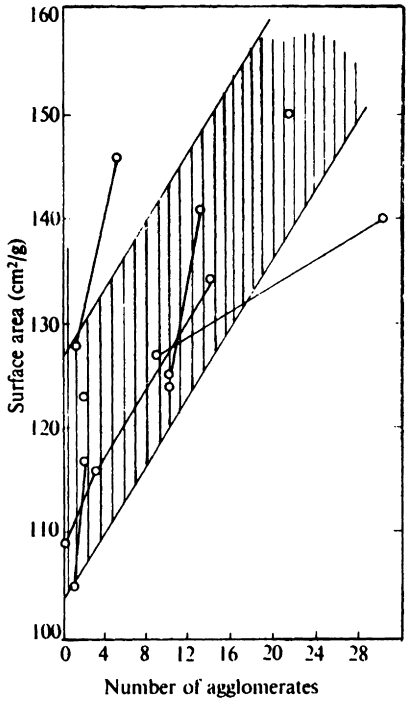


FIG. 110. Dependence of surface areas upon the number of agglomerates in grain samples for the durability test. (Sewell.)

[15] *J. Amer. Ceram. Soc.* **50**, (2), 108–111 (1967).

represent acidic functions. When molten mixtures of Na hydroxide and Na nitrate react on the surface of a resistant glass as is, such as zirconium silicate, the corrosive leaching shows a tenfold increase in chemical durability when $NaNO_3$ is added to the NaOH melts (maximum concentration showing this effect is about 60%). These and similar other observations are important for an understanding of the behavior of Zr silicate crucibles in their unusually good corrosion stability to molten alkali hydroxides when nitrate is added as a "diluent." This improving effect may last for several minutes, i.e., as long as dissociation of the nitrate has not evolved free alkali in the mixed melts.[16]

429. K. Rehm[17] reports on the application of titrimetric and flame-photometric methods in testing glass medical ampuls, for their hydrolytic surface resistivity (as specified in the standard test DIN, 52 329); under the latter method it is even made possible to examine individual samples (of "Fiolax" glass), with a good agreement of results verified by one, or the other method.

430. H. E. Schwiete, M-a. Schemmel, and Th. Langauer[18] made extensive measurements of *gas adsorption* on the surface area of glass grits of considerably diversified chemical composition, by the volumetric way, especially for argon, the fundamental problem, as a function of pressure and temperature, and the isosteric heat of adsorption as based on the theory of St. Brunauer, P. H. Emmett, and E. Teller[19] over the range $p/p_s = 0.05$ to 0.30, and the isotherms of adsorption for two carefully chosen alkali silicate glasses, at $-196°$ and $-24°C$ (temperature of a mixture of ice and NaCl). Evidently, the chemical composition of the glasses exerts a distinct influence on the forces interacting between adsorbent and adsorbate. The change in the heat of adsorption in the system glass boundary/adsorbed H_2O layer is higher for Na silicate glasses than for corresponding K silicate glasses. The specific surface of glass grits which had been previously used in the investigations of Žagar and Horina (see above ¶ 422), was calculated with good reproducibility, but considerable differences in the absolute surface data appeared, most probably introduced by aging effects in the glass samples.

431. S. K. Dubrovo, A. D. Shnypikov, L. G. Shnypikova, and S. D. Spirina[20] prepared an alkali–zirconium silicate glass containing lithia and La_2O_3, SrO, and BaO, of a specifically high durability in alkaline solutions, and of a high thermal shock resistance in the standard quality specification (USSR, Pat. No. 911, 959)

[16] Cf. A. Lundén, *Corros. Sci.* **1**, (1), 62–64 (1961); J. C. Casanova, *Bull. Soc. Chim. Fr.* pp. 429–434. (1959).

[17] *Pharm. Ind.* **29**, 868–869 (1967).

[18] *Glastech. Ber.* **39**, (1), 14–19 (1966).

[19] *J. Amer. Chem. Soc.* **60**, 309–319 (1938).

[20] *Steklo Keram.* **23**, (5/6), 232–235 (1966), (Engl. transl.).

belonging to the best hydrolytic class, according to DIN standard 52 322, with a very low weight loss (2.5 mg/dm^2 when tested for 3 hours in a solution of 0.5 *N* NaOH + 0.5 *N* Na_2CO_3 brine).

432. Since we have repeatedly referred (cf. Vol. II.A. ¶ 397; Vol. VII. ¶ 599, 896 ff.) to the use of *radioactive tracer* techniques for the study of *self-diffusion* of radioactive isotopes, we mention the use of these elegant methods here only briefly in connection with the leaching stability of glass surfaces as a standard testing for chemical durability. We first refer to a publication by E. Baier, E. Deeg, and H. G. Constabel,[21] who examined the adsorption of orthophosphoric acid on ternary borate glasses using nuclid ^{32}P as the tracer element. Valuable general remarks on the radioactive tracer techniques for chemical durability testing of different glasses were also contributed by A. D. Shnypikov, I. S. Kirin, and Yu: K. Gussev,[22] specifically on β-radiation measurements of solutions containing leachates made from neutron-activated glasses, by water, acids, and alkaline brines. Systematic comparison tests made it evident that the results of this method are in a good agreement with those obtained from the commonly used chemical-analytical methods. The β-radiation methods are a reliable help in the direct analytical control of true solubility after the standard glass grit extraction methods (leaching in water, 1 *N* H_2SO_4 or 1 *N* NaOH, at 90°C) as was demonstrated for a high-resistance 2% La_2O_3- and 14% ZrO_2-containing special glass (DG 3) for a 3-hour treatment at 90°C. For the latter glass, it is quite particular that the ratioactivities of the leachates from this ZrO_2 silicate glass indicate by about six times higher alkali durability than the other methods do when the water and acid leachabilities are about the same for all the other glasses.

LEACHABILITY AND WEATHERING PHENOMENA

433. For comparison and analysis, Fr. R. Bacon and Gl. I. Calcamuccio[23] studied differences between the chemical durability of common Na – Ca silicate glasses that had been cured in moist air and that had been cured in dry air, before they were tested. Particular attention was given to changes in the surface layer, of bottle glass exposed, while in the molds, to moisture-containing compressed air during the blowing process. With increasing time and temperature, and with an increasing adsorbed water content of the air, the durability of the bottle glass is significantly reduced. In this phenomenon, it does not make much difference whether the bottle surface has been treated in an SO_2 gas atmosphere. In all these tests dry oxygen and nitrogen

[21] *Glastech. Ber.* **39**, (3), 136–138 (1966); **39**, (11), 496–499 (1966); **39**, (12), 530–538 (1966); **40**, (1), 18–23 (1967); cf. VII. ¶ 897.

[22] *Steklo Keram.* **23**, (12), 12–15 (1966); **23**, (11/12) 644–645 (1966), (Engl. transl.).

[23] *Bull. Amer. Ceram. Soc.* **46**, (9), 850–855 (1967).

behave the same way as dry air (with a dew point temperature of −33.3°C). All signs in the behavior of the bottle glass indicate that after a definite time an equilibrium is established between the rate of alkali diffusion through the glass surface and evaporation of water from it, causing a "standing" alkali concentration of free alkali on the glass surface which, however, evaporates Na as long as the glass is in contact with the inner surface of the hot blowing mold during blowing of the finished bottle. On cooling, some alkali is redeposited on the glass. It is of practical interest that it is possible to enhance the surface resistance of the glass when the shaping and annealing is done in dry air and during exposure.[24]

434. We recommend the comprehensive report by Fr. R. Bacon,[25] who includes common alkali–Ca silicate glasses, borosilicates, silica, Vycor, and a special series of glasses with tabulated composition data and those of different durability reactivity, as subject to the alleged improvement effects of treatment with SO_2 gas ("sulfuring").

435. *Radioactive tracer* measurements of the self-diffusion of $^{22}Na^+$ in NaCl- and Na_2SO_4 (2.02 and 3.64%, respectively) containing Na disilicate glasses by H. Schäfer and H. Maywald[26] confirm the presumption that a very low content of those salts would be sufficient to cause phase unmixing and enrichment of the alkali ions as well as of Cl^- and SO_4^{2-} anions in heterogeneous local areas, thus increasing tendencies for localized devitrification effects, as W. Vogel and G. Gerth[27] described them, by highly disordered domains which primarily increase the intensity of ionic diffusion and secondarily enhance devitrification,[28] but not by activated mobility of the cations alone.

436. F. K. Aleĭnikov (Aleinikovas) and I. I. Zhitkyavichyute[29] presented an extensive report on the *free-alkali* durability of silicate glasses among which those containing ZrO_2 and SnO_2 show the highest resistivity data in NaOH solutions (over a wide range of concentration). They also analyzed the formation of a thin reaction surface layer on the glass by treatment in which amorphous and crystalline deposits of the hydroxides of the divalent metals are observed in the electron microscope and identified by X-ray diffraction data and diagrams.

[24] W. K. Berthold, U.S.A. Patent Nos. 2, 273, 778 (Feb. 1942); Fr. R. Bacon, U.S. Patent Nos. 3, 215, 575 (Nov. 1965).

[25] *Glass Ind.* **49**, (8), 438–439, 442–446 (1968); **49**, (9), 494–499 (1968); **49**, (10), 554, 557–559 (1968).

[26] *Glastech. Ber.* **40**, (7), 253–257 (1967).

[27] *Z. Chem.* **2**, 261–274 (1962).

[28] Cf. III.A. ¶ 32, footnote 34; 64, footnote 96; see also W. Vogel, *Silikattechnik* **16**, (5), 152–158 (1965).

[29] In the book "Glass-Forming Systems and Materials," (Yu. Ya. Eĭduk, ed.), pp. 151–167, Zinatne Publ. Off., Riga, 1967.

437. A more specialized free-alkali-induced corrosion of heavy Crown glass by LiOH, NaOH, KOH, NH_4OH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, was described by M. Inoue and Sh. Tsuchihashi,[30] who used the optical interference method to measure the progress of the corrosion. With exception only of NH_4OH and $Ca(OH)_2$, the corrosion action of the hydroxides with monovalent R^+ ions was higher than it was with $R(OH)_2$. Curves demonstrating the correlation between the depth of corrosion and the time periods of exposure are increasingly of parabolic shape, up to pH = 10.0 and above 10.5 are approximately linear. The curves showing the correlation of depth corrosion as a function of pH show a maximum for pH = 10.0 to 10.5. Of all the hydroxides investigated, NH_4OH was the most corrosive; $Ca(OH)_2$ had the least effect.

438. We come back to the work done by R. W. Douglas and T. M. M. El Shamy[31] on the reaction kinetics of glass leaching in water or in aqueous solutions which have been characterized by a simultaneous occupancy of surface sites by hydrogen, protons, or alkali cations as though these were clearly discernible and separable processes. During the reactions, the concentration gradients of diffusion are determined by the variation of the diffusion coefficients with concentration, but also by boundary conditions, namely the concentrations at the leached layer boundary to the leached layer solution boundary, the sites on the surface being occupied by H^+ and R^+ ions. Above the critical pH the concentration in H^+ ions in the solution is so low that those sites are occupied by R^+ ions, which increases the alkali concentration at the boundary and slows down the diffusion. Removal of silica from the solution is increased with a rising pH, thus exerting an inverse influence on diffusion and tending to decrease the thickness of the silica-enriched layer. In the measure that silica is removed, alkali is brought into solution to occupy the surface sites. The characteristic diagrams, Figs. 111 and 112, illustrate for potassium silicate glasses those effects of long-time-period water leachings.

439. Newer studies were made by R. W. Douglas and R. Das[32] on the water leaching of ternary alkali silicate glasses of the type $R_2O, 4SiO_2$ and certain glasses in which a portion of the alkali (5%) was substituted by di-, tri-, and tetravalent metal oxides. In previous studies by Douglas and Rana, as well as in the new series, the normal $\sqrt{t}$ law for the leaching amounts was valid for all those glasses in a first time period, later followed by a linear increase for the amounts of R_2O and SiO_2. In every case, the ratio of the leached amounts, R_2O/SiO_2, was higher than the ratio in the original glasses, and the law is written $Q = a\sqrt{t} + bt$. The assumption was made

[30] *J. Ceram. Ass. Jap.* **75**, (9), (865), 264–270 (1967).

[31] *J. Amer. Ceram. Soc.* **50**, (1), 1–8 (1967); cf. II.A. ¶ 289 f. 304; VII.A. ¶ 531.

[32] *Phys. Chem. Glasses* **8**, (5), 178–184 (1967).

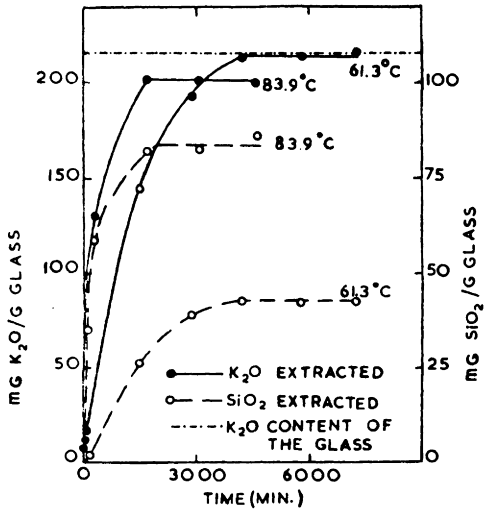


FIG. 111. Extraction of alkali and silica in long-time water leaching runs on glass of composition $15K_2O$, $85SiO_2$. (Douglas and El-Shamy.)

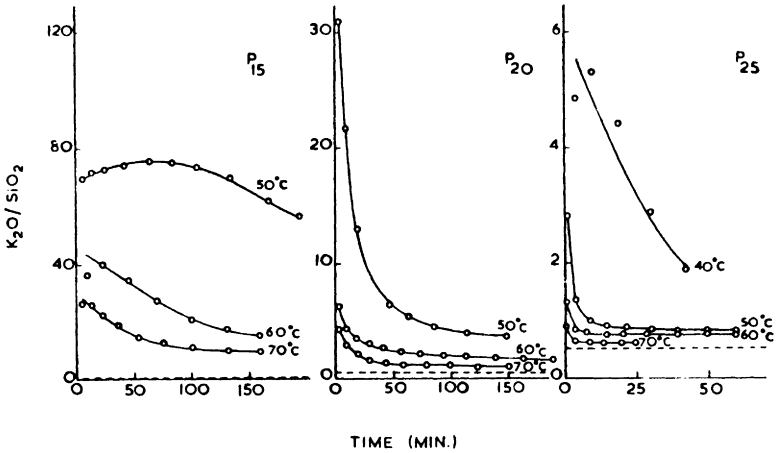


FIG. 112. Effects of time, temperature, and composition of glass on the total ratio K_2O/SiO_2 extracted in water leaching runs. (Douglas and El-Shamy.)

that during leaching reactions an alkali-impoverished layer is formed. When a third oxidic constituent was introduced, it was observed that it was leached out in a linear proportion to SiO_2, i.e., the leached surface layer is higher in the concentration of the third component than it is in the original glass. Additional model concepts were not able to establish a direct correlation between chemical durability and electrical

conductivity; therefore, it was concluded that the reactions do not correspond to an elementary cation exchange for which the diffusion of the alkali ions through the glass is the speed-determining factor.

440. C. R. Das[33] described a convenient apparatus for the performance of accurate leaching reactions of glass grits or "bits" and for temperatures up to 100°C, even for prolonged periods. The results of measurements with variable leaching solutions made it evident that more silica and less alkali are extracted by solutions with a higher pH, than by those with lower pH. With particular care, C. R. Das and S. A. Katrekar[34] developed a method for an accurate determination of the specific surface of powdered glasses, enamels, and even minerals based on the optical density of the blue color of reduced ammonium silicomolybdate formed by the reaction of silica extracted by an alkaline solution from silicate glass. This method achieved satisfactory reproducibility and works very rapidly in practice, e.g., to control the quality of glass enamels (cf. ¶ 508ff., 583).

441. Another fundamental problem that of practical determination of the rate of Na^+ migration in the presence of divalent cations (Mg, Ca, Ba, Zn, Cd, Pb) in silicate glasses, was studied by R. Terai and T. Kitaoka,[35] over a temperature range from 200 to 450°C by using radioactive ^{22}Na tracer techniques. The self-diffusion coefficients of Na^+ ions and the electric conductance of glasses of the type $Na_2O-RO-SiO_2$ are decreased when effective diameters of the exchanged divalent cations increase, indicating that the polarization and field strength of these cations determine to a high degree the migration of the Na^+ ions. The Nernst–Einstein (cf. ¶ 422) equation delivers for the correlation factor f, the numerical values of 0.2 to 0.3 for different glasses, indicating an ion transport over empty structural holes or even intermediate framework. These mechanisms are the same for the transfer which is observed in binary Na silicate glasses, and is not ruled in any significant measure by the nature of the divalent cations.

442. For lithium silicate glasses the water leaching process is coordinated to phase-separation phenomena as S. Kumar and A. K. Maitra[36] observed, since, in the structure of such a glass (e.g., with 7 mole % Li_2O content) the small Li^+ cations are nearly completely hidden in the silica matrix. With an increasing content of Li_2O, however, the matrix is reduced and the extractable alkali is strongly increased in the leachates. These steric effects are also very strong for Li borosilicate glasses. Water-leaching can become so intense that after an "exhaustive" leaching, the extraction

[33] *Bull. Centr. Glass Ceram. Res. Inst.* (*Calcutta*) **14**, (1), 5–11 (1967).
[34] *Bull. Centr. Glass Ceram. Res. Inst.* (*Calcutta*) **15**, (4), 110–113 (1969).
[35] *J. Ceram. Ass. Jap.* **76**, (11), 393–399 (1968); cf. II.B. ¶ 155.
[36] *Trans. Ind. Ceram. Soc.* **27**, (2), 69–75 (1968).

residues will consist of 92% silica and only traces of Li_2O. On the other hand, a substitution of B_2O_3 by Al_2O_3 causes an increasing chemical durability by about two orders of magnitude.

443. R. H. Doremus[37] observed in Pyrex glass the mutual interdiffusion of Na^+ and Ag^+ cations as if it were influenced by a two-phase structural phase unmixing. It was found that the introduction of Ag^+ ions does *not* affect the diffusion coefficient of Na^+, but that the diffusion of Ag^+ ions slows down in the measure in which the concentration in Ag^+ in the glass decreases, most probably by a preferred adsorption of Ag^+ ions on the silica phase. Evidently, the rate of exchange between the two phases is reduced when the Ag^+ concentration decreases. The diffusion coefficient for tracer-doped Na^+ was found to be different from that calculated from the electric conductance. Similar phenomena are known from other two-phase glasses.

444. Older problems of critical *cleaning* degrees of *glass surfaces* by evolution of hydrogen *in statu nascendi* from Na metal solutions in liquid ammonia (at −76°C) and sodium films in hot state are solved by studies of S. Naiditch and J. E. Wreede.[38] This very efficient method is of eminent importance for eliminating contamination from glass surfaces and is of great practical value for other surface treatments in combination with alkyl chlorosilane and vacuum heating.

445. We bring such practical problems to the foreground because of their great similarity to those of the elimination and disposal of radioactive waste residues. In this connection M. N. Elliot and D. B. Auty[39] contributed a new method concerning the trace solubility of Sr^{2+}, Cs^+, Ce^{3+}, and Tb^{3+}, by simple leaching at 30° and 60°C and determination of the activity of the solutions by the γ spectrometer. The matrix glasses may be borosilicates or phosphates; the results are given as "leaching factors" defined as the reciprocal value of the depth of penetration (its dimension is equal to week/cm). These factors are about the same for Cs^+ and Sr^{2+}, but by a factor of 100 higher for Ce^{3+} and Tb^{3+}. Arranged in the order of increasing leach factors, the series is $F_{Na} < F_{Si} < F_B < F_{Cs}$, $F_{Sr} < F_{Ce} < F_{Tb}$. When the temperature is increased from 30° to 60°C the leaching factor decreases by about one order of magnitude. For a given borosilicate glass, Elliot and Auty determined that the leaching factor was $= 1$ to 4×10^6, for a phosphate glass it was between 10^5 and 10^6. For Si, B, Na, and P the surface of the leached silicate layer proved to be rich in oxidic fission products.

446. We may here note some practical characteristic data contributed by E.

[37] *Phys. Chem. Glasses* **9**, (4), 128–132 (1968).
[38] *J. Vac. Sci. Technol.* **5**, (2), 54–60 (1968).
[39] *Glass Technol.* **9**, (1), 5–13 (1968).

Schiewer, W. Lutze, and W. Heimerl[40] on the fixation of radioactive wastes by cation exchange and adsorption, not on synthetic glasses, but on natural tuff-type rocks called "Fibrolite" (from the Eifel Mts., Germany) which proved to be eminently active for just this problem of radioactive waste elimination. Also, other types of glass (synthetic compositions preferably) are discussed in this remarkable article mentioned here, although it belongs with our problem fields in Vol. I.C. ¶ 181, 287, and chiefly Vol. IV.B. ¶ 106 Footnote 195, and recently Vol. VI.C. ¶ 5, 354, 504, called 'scavenging" measures.

447. G. H. Frischat, to whom we owe valuable observations and numerical data on the application of *radioactive tracer methods* in glass science and practice contributed so many details in this wide field that we must refrain from repeating here. However, the reader may find in the following references some indication of the special aims of certain publications and how to find the details in Vol. VII.

G. H. Frischat and H. F. Oel,[41] on the "residual activity method for the determination of self-diffusion coefficients of solids" (cf. Vol. VII. 164 ff.);

G. H. Frischat and H. J. Oel,[42] on transport mechanisms in glassy and crystalline $Na_2O \cdot 2CaO \cdot 3SiO_2$ (cf. Vol. VII. ¶ 119, 166 ff.);

G. H. Frischat,[43] on ^{22}Na and ^{45}Ca volume and grain size diffusion in polycrystalline $Na_2O \cdot 2CaO \cdot 3SiO_2$ (cf. Vol. VII. ¶ 119, 166 ff.);

G. H. Frischat,[44] on the determination of effective grain boundary diffusion in polycrystals of small crystallite dimensions (cf. Vol. VII. ¶ 119, 166 ff.);

G. H. Frischat,[45] sodium self-diffusion in sodium aluminosilicate glasses (cf. Vol. VII. ¶ 166 ff.);

G. H. Frischat,[46] textural changes of polycrystalline $Na_2O \cdot 2CaO \cdot 3SiO_2$, on annealing (cf. Vol. VII. ¶ 166 f.);

G. H. Frischat,[47] a simple method for determination of exchange profiles in glasses, applying the microindentation test (cf. Vol. VII. ¶ 901);

G. H. Frischat,[48] cation self-diffusion in silicate glasses (Vol. VII. ¶ 228).

448. Entirely practical aspects of rinsing tumbler glass were contributed by

[40] *Glastech. Ber.* **44**, (9), 377 ff. (1971).
[41] *Z. Angew. Phys.* **20**, (3), 3–7 (1966).
[42] *Glastech. Ber.* **39**, (2), 50–61 (1966).
[43] *Ber. Deut. Keram. Ges.* **44**, (5), 232–239 (1967).
[44] *Z. Angew. Phys.* **32** (4), 281–287 (1967).
[45] *Glastech. Ber.* **40**, (10), 382–385 (1967).
[46] *Ber. Deut. Keram. Ges.* **46**, (6), 316–320 (1969).
[47] *J. Noncryst. Solids* **3**, 407–409 (1970).
[48] *Glastech. Ber.* **44**, (3), 93–98 (1971).

S. Lohmeyer.[49] His observations of the test rinsing stage covered leaching of the glass surface in circulating and in stagnant water; the hydrolysis test of glass grits and powders, with very instructive micrographs and interferometric diagrams; the primary deposition of calcium phosphate layers in spotwise electronographs, and scanning micrographs of scratches on glass surfaces. Steam condensation on glass surfaces is highly detrimental to the tumbler surfaces, while variations in the degree of hardness of tap water are of relatively little importance. Additions of detergents to the rinsing water often make it more corrosive than pure water that has been "neutral-softened," and completely deionized water is even more aggressive. When polyphosphates are applied, swelling layers and intercalations of phosphates are observed, the more the higher the temperature, but there is no decomposition of polyphosphates to form aggressive ortho- or pyrophosphates. Cut-ground surfaces are considerably more sensitive to aggressive rinsing solutions; the corrosion is as a rule starting from local surface defects. Fire-polished, gas- and silicone-treated surfaces withstand corrosion in water only when the water is not warmer than 55°C.

449. *Borosilicate glasses* were tested by N. M. Pavlushkin and A. K. Zhuravlev[50] for their stability and solubility in boiling water; glasses of the ternary system $PbO-B_2O_3-SiO_2$ show a pronounced tendency for unmixing with increasing concentrations in silica above 30 mole % and in boron trioxide above 65 mole %.

Concerning the determination of ion concentration profiles in surface layers of leached ("swollen") glass electrode membranes, refer again to our report in ¶ 368 from the publication of H. Bach and F. G. K. Baucke.[51]

450. How glass surfaces are modified by the action of electron radiation beams from the electron microprobe, H. Estour[52] reviewed extensively. The most striking phenomenon is a rapid volatilization of sodium and potassium from the glass surface, combined with a rapid decrease of intensity in the secondary K emission response. Calcium, barium, and even zinc, are volatilized in the same manner,[53] e.g., from the surface of television tube glass surfaces, whereas, aluminum and silicon are enriched on the surface, as a consequence of their low mobility. Mg^{2+} ions show an intermediate reaction to the electron bombardment when exposed in glass to the electron microprobe over certain long periods.[54]

[49] *Glastech. Ber.* **43**, (3), 101–115 (1970).

[50] Izv. Akad. Nauk S.S.S.R. *Neorganich. Mater.* **5**, (3), 481–484 (1969).

[51] *Electrochim. Acta*, **16**, 1311–1319 (1971).

[52] *Verres et Refract.* **25**, (1) 11–17 (1971).

[53] Cf. M. P. Borom and R. E. Hanneman, *J. Appl. Phys.* **38**, (5) 2406–2407 (1967)

[54] Cf. J. I. Lineweaver, *J. Appl. Phys.* **34**, (6) 1786–1791 (1963); on the microprobe action onto K–Sr silicate glasses, cf. A. K. Varshneya, A. R. Cooper, and M. Cable, *ibid.* **37**, (5) 2199 (1966).

451. On the reaction of hydrofluoric acid, as the gas, and in dilute solutions with glass surfaces, J. Suire[55] presented an elaborate discussion of the conditions for an anion interchange of the type $OH^- \rightleftharpoons F^-$, in the light of W. A. Weyl's theories. By mineralogical microscopic methods, the following compounds were identified as reaction products with different commercial glasses; Na_2SiF_6; K_2SiF_6; $MgSiF_6 \cdot 6H_2O$; $MnSiF_6 \cdot 6H_2O$; $PbSiF_6 \cdot 4H_2O$, perhaps, also as a crystalline precipitate: $(NH_4)_2SiF_6$.[56] Glass of a freshly broken fracture surface appears for a few minutes to be inert under etching, but then, in an atmosphere of 66% relative moisture content, typical corrosion centers appear, indicating the condensation of water droplets which is indispensable for acceleration of the reaction. Experimentally, such observations are difficult to reproduce because of the many disturbance factors involved, e.g., the lack of homogeneity of the glass structure, and the presence of innumerable local surface defects.

452. The question of whether annealed and nonannealed glass powders may differ in chemical durability was examined by D. L. Rothermel[57] by observing how a blow with a pointed instrument, short of shattering it, produces strains and locally increased density, immediately below the surface of where the glass was struck. The strain alone can be removed by annealing,[58] but other indications made evident that weathering occurs more slowly in the grooves formed by scratches than in the surrounding areas, presumably by compaction in the strained glass.[59] Glass powders examined in the usual way for durability under Na^+ leaching were tested extensively by Rothermel who observed some alkali volatilization which gives an easily misleading picture when the glass has not been rinsed in water and acetone before annealing. As the end result, it was concluded that there is *no* definite tendency for the annealing to develop stresses large enough to alter the Na^+ leachability during preparation of the samples, but the alkalies migrate during annealing to the glass surface, creating a higher Na^+ concentration in the surface layer from which it is extracted during the leaching test the longer it is applied, as a normal alkali loss phenomenon.

453. The mathematical treatment of the immediate results from glass corrosion experiments which is *de facto* a problem of modern *statistical* calculus, is particularly suitable for computer evaluation when large numerical material is available; in this

[55] *Silicates Industrs.* **36**, (3) 73–79 (1971); 101–104. (1971).

[56] Cf. V. Gottardi and G. Bonetti, Proc. Symp. Resistance Mecan. du Verre, Florence, 1961, pp. 393–406.

[57] *J. Amer. Ceram. Soc.* **54**, (4), 218 (1971).

[58] Cf. R. A. Hatch's observation, 1944.

[59] Cf. J. D. MacKenzie, *J. Amer. Ceram. Soc.* **46**, (11), 461–470 (1963).

understanding it was discussed extensively by D. K. Hoganson and J. H. Healy.[60] Starting with specific glasses as paradigmata, taken from practical experience (e.g., TiO_2-, ZrO_2-, and CoO-containing borosilicate glass) and a normal leaching treatment with a 10% HCl solution, the weight losses of glass rods were measured after they had been under constant temperature for a definite time period. The results showed convincingly that there is a linear correlation between the logarithms of the weight losses and the reciprocal temperature for a constant time period of leaching, but also another linear correlation with the logarithm of the time exposure, at constant temperatures. From the combination of these correlations a multiple regression equation could immediately be derived, with a correlation coefficient of 0.97. The same calculation was then applied to leaching experiments with different acids (namely, HCl, H_2SO_4, HNO_3, and H_3PO_4). The results were evaluated again with a correlation coefficient of about 1.0. The other constants of the regression equation show a function relation with the chemical nature and concentration of the leaching acid solution, and the nature and composition of the glass itself. Figures 113 and 114 illustrate these correlations.

454. Other fundamental derivations for an analysis of mechanisms and kinetics of the reactions which alkali silicate glasses undergo with water at elevated temperatures were developed by J. Hlaváč and J. Matej,[61] who distinguished two different

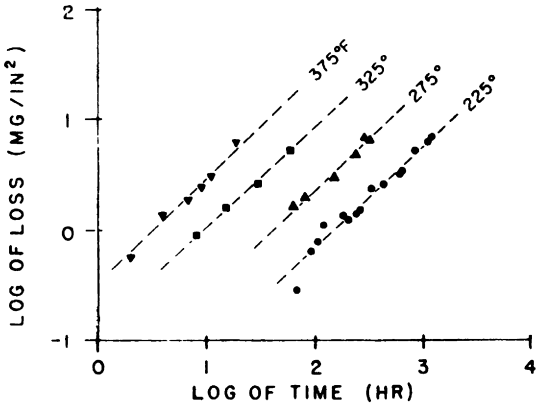


FIG. 113. Plot of data on corrosion–time axes, with constant temperature lines visually determined for a test glass "G" (composition between 60 to 70% SiO_2; 0 to 2% TiO_2; 5 to 8% ZrO_2; 3 to 6% B_2O_3; 0 to 3% Li_2O; 12 to 16% Na_2O; 0.5% CoO; 1 to 2% F_2, all in weight %) in dilute (10%) HCl solution. (Hoganson and Healey.)

[60] *J. Amer. Ceram. Soc.* **45**, (4), 178–181 (1962).
[61] *Silikaty* **7**, (4), 261–265 (1963).

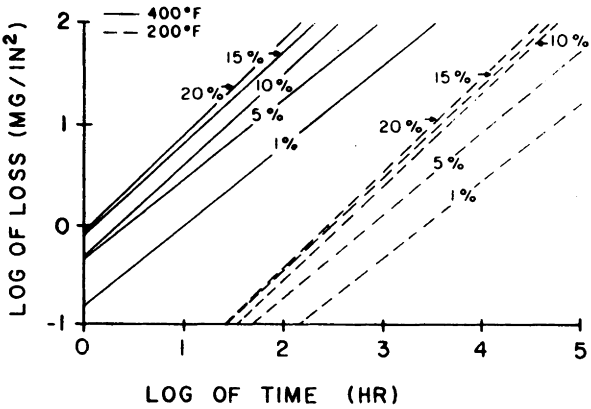


FIG. 114. Plot of data for the calculated relation of corrosion of test glass "G" in various concentrations of HCl solution. (Hoganson and Healey.)

processes in the leaching reactions: (1) a diffusion of alkali ions from the glass into the water to form a silica-enriched surface layer on the glass which tends asymptotically to approach a final limit value; and (2) a stationary state characterized by an equilibrium of initial partial dissolution of the silica-enriched layers, in counterweight with a stationary rebuilding of additonal silica layers. For both antagonistic reactions, elementary equations could be established to illustrate the time function of the total process. The same authors[62] demonstrated the calculation of the kinetic equations as based on an example from practical experience with a satisfactory agreement between the theory and the experimental data for hot-water leaching. For a Na–Ca silicate glass, the authors examined the validity of their calculation method for variable pH of the aqueous solutions over the wide range from pH = 1.6–12.5 at 100°C.[63] The best agreement of theory and experimental data was in all cases confirmed for alkaline solutions, whereas in acid solutions, certain anomalies appeared as a nonlinear functional correlation; the assumptions of a linear time function of the corrosion reactions with silica could not be confirmed in every case. We may finally emphasize theoretical deductions made by Z. Boksay, G. Bouquet, and S. Dobos[64] on the evolution of stationary alkali concentration profiles during glass extraction with water which follows in its diffusion function the second Fick law. This process was demonstrated for extraction profiles in near-surface layers for a potassium silicate glass to confirm an excellent agreement of experimental leaching data with the postulates of theory (cf. on previous observations, Vol. II.B. ¶ 155, footnote 260).

[62] *Silikaty* **10**, (3), 235–245 (1966).
[63] *Silikaty* **11**, (1), 3–16 (1967).
[64] *Phys. Chem. Glasses* **8**, (4), 140–144 (1967); **9**, (2), 69–71 (1968).

CHEMICAL RESISTIVITY PHENOMENA OF GLASSES EXPOSED TO CORROSIVE ACIDS

Autoclave Tests

455. Although some details of the following must be understood in connection with phenomena of devitrification and crystallization from glass melts, as in the production of so-called Pyroceram (glass-ceramics) which we discussed explicitly in Vol. III.A., it is highly instructive to consider here some selected glass-forming systems from the practical viewpoints of corrosion and chemical durability. B. Löcsei[65] studied the important system $Na_2O-CaO-MgO-Al_2O_3-SiO_2$, in which the glasses show a chemical durability of remarkably good quality which is of particular interest here, and for glass-ceramics from which plagioclases (Ca – Na feldspars) and diopside are typical crystallization phases after nucleation and crystal growth.

456. Of optimum mechanical properties are the complexes in the polynary oxidic system along the tie-line between the eutectic points of the partial system $NaAlSi_3O_8-CaAl_2Si_2O_6-CaMgSi_2O_6$. The chemical resistance of the crystallization products is a function of composition and the amounts of crystalline phases; the structural compaction increases with time. The chemical durability against hot mineral acids is excellent, namely, below 6.0 g/m^2 in 24 hours, i.e., of the first Class of the International Corrosion Specifications, and in the upper positions of Class II. It is very interesting that after prolonged exposures to acids a *passivation* effect is reached, i.e., the weight loss curve gradually decreases asymptotically reaching a minimum below 0.5 g/m^2 per 24 hours, independent of the nature of the acid solution used in the experiments. An instructive diagram showing the influence of the percentage contents in crystalline phases for such glasses (using a 10% HCl solution) is seen in Fig. 115. The products used by Löcsei in his experiments were commercially known under the trademark "Minelbite."[66] The crystallization in this special case was induced by addition of heavy metal sulfides as the mineralizing agents.

457. Returning to acid corrosion problems, we refer to recommendations by F. B. Adams, M. E. Nordberg, and H. V. Walters[67] of flame-photometric determination of the extracted alkalies after reaction of the testing sample with a 5 mole HCl

[65] Symp. on Nucleation and Crystallization in Glasses and Melts, pp. 71–74, Amer. Ceram. Soc., Columbus, Ohio, 1962.

[66] Cf. III.A. ¶ 39, footnote 48; specifically ¶ 46, footnote 58 to which we refer.

[67] *Glass Technol.* **5**, (4), 136–141 (1964).

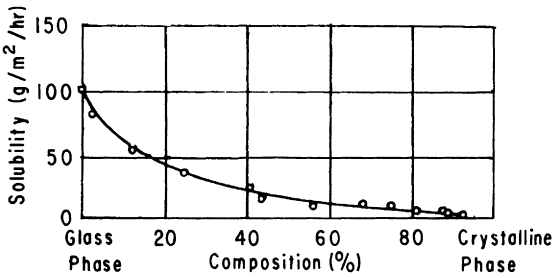


FIG. 115. Chemical resistance of matrix glass in Minelbite glass-ceramics to 10% HCl solution, as a function of the degree of crystallinity. (Löcsei.)

solution at 95°C for a treatment lasting 24 hours, as demonstrated for a series of commercial glasses of much different composition types, either tested in sheets and plates, or as a grit of 0.30 to 0.42 mm in diameter, applied in stagnant and stirred liquids. Flame-photometric determinations of the alkalies are much more accurate than the simple weight loss controls. It is characteristic that for the surface durability examination of Na-containing silicate glasses, the flame-photometric results observed with HF-pretreated plates were considerably above those of fire-polished surfaces.

458. A systematic development of glasses derived from the Na–Ca silicate compositions by modifying substitutions was made by E. P. Rusetskaya and N. N. Ermolenko[68] in which inexpensive nepheline syenite wastes could be made valuable as an essential constituent of the glass batches, with corrective additions of Al_2O_3, ZrO_2 in amounts of 2 to 5 mole % effecting essential improvement of acid durability of the glass and the stability against devitrification. Corresponding experimental investigations starting with the basic nonsilicate system $MgO-B_2O_3-Al_2O_3$ (also with CaO addition) were made by the same authors[69] in the production of quality fibers and glass wool, including a considerable improvement of resistivity against acid corrosion in glass, the composition of which was very near to the binary eutectic of the partial system $CaO \cdot B_2O_3 - 2CaO \cdot B_2O_3$ (fusion point 1132°C[70], whereas the other compositions of the ternary system field were more intensely corroded.

[68] In the book "Glass-Forming Systems and Materials," (Yu. Ya. Eïduk, ed.), pp. 87–90, Zinatne, Publ., Riga, 1967.

[69] Reference 68, pp. 91–94.

[70] Cf. D. S. Belyankin, V. V. Lapin, and N. A. Toropov, "Phys. Chem. Systems of Silicate Technology, 2nd ed., pp. 117, Gosud. Izdat. Lit. po Stroit. Mater., Moscow, 1967.

459. For very similar purposes of the glass fiber industry, M. A. Matveev and Yu. M. Solodukho[71] described an entirely alkali-free Al borosilicate glass with 10% B_2O_3 content and glasses in which B_2O_3 is replaced by TiO_2 and SrO. As a matter of fact, introduction of TiO_2 improves the chemical durability markedly and raises the devitrification temperatures and the mechanical strength; addition of MgO or even that of SrO would do the same. More detailed experimental studies were made by O. V. Mazurin, A. S. Toteshova, and G. T. Roshkovora[72] for low-in-alkali borosilicate glasses in which a part of the basic B_2O_3 was replaced by Al_2O_3. The hydrolytic durability proved to be essentially improved by this substitution; so was the correlation between viscosity and transformation range temperatures. Other studies by Mazurin, Toteshova, and M. V. Strel'tsinova[73] concerned the use of special borosilicate glasses low-in-alkali for the production of Mo and Wo sealing glasses. (cf. ¶ 405 f.). The systematic replacement of B_2O_3 in increasing amounts show that alkalies strongly influence the inherent tendencies to unmix.

460. Pyrex-type glass, when exposed to an *autoclave* (low-pressure) treatment above 100°C, shows the characteristic exfoliation of finest scales often described in sterilization autoclave practice. These scales are so thin (only in maximum 0.3 μ, scales in diameter 3–30 μ) that they can, according to M. B. Volf[74] be isolated only by freezing them into ice, then evaporating the water in a vacuum of 10^{-4} torrs ("lyophilization", for pharmaceutical purposes). With the electron microscope and a replica technique (and Au–Pd shading) one may pursue the development of such scales and find that volatilization of B_2O_3 from the surface of the "neutral glass" and crystallization of cristobalite during the thermal treatment acts in the same direction with the volatilization of residual alkali. The endangering evolution of the silica scales is a serious problem for Vycor or Pyrex glass and for ampule glasses used for blood and serum. All are of the low-in-alkali type when the ratio Si/O is above 0.4.[75]

461. Observations of *changes by weathering* of differently resistant modern and ancient glasses are, to a high degree, similar to those of artificial corrosion

[71] *Silikattechnik* **19**, (2), 51 (1968).

[72] *Steklo Keram.* **19**, (5), 131–132 (1968).

[73] *Stéklo Keram.* **19**, (4), 100–101 (1968).

[74] *Silikattechnik* **20**, (5), 155–158 (1969).

[75] See on this critical ratio and its significance for lyophilization: M. L. Huggins, K. H. Sun, and D. O. Davies, *J. Amer. Ceram. Soc.* **26**, (1), 4–11 (1943), who defined the ratio Si/O in the symbol $N_{Si} = \left(\frac{SiO_2}{M_{SiO_2}}\right) \Big/ \left(\frac{n}{M_{R_mO_n}}\right) R_mO_n$ (as a function of n, number of oxygen atoms in the formula of the oxides, m, that of the metallic atoms. The oxides are in mass %, $M_{R_mO_n}$ are their molecular weights).

phenomena; they were studied more recently by R. G. Newton[76] e.g., in 430-year-old cullet which had been buried in moist soils. We need not describe the many morphological details, but should realize how such weathering crusts are developed, either as thick crusts with many faulted layers, or, in another extreme, as rather smooth nearly normal surface layers. It is very difficult reliably to coordinate these highly variable formations to the chemical compositions of the original glass. We may refer to other recent publications, e.g., by R. Strienitz[77] and by R. Wollast, P. Brennet, and A. Jelli,[78] which detailed the transition of an Na – Ca silicate glass into weathering crusts not unlike the ancient glass crusts mentioned above, in corrosive media of high acidity (in the first publication concentrated H_2SO_4 was applied).

462. Such probes are of great practical significance, e.g., for glazed ceramics as used in the construction of denitration towers, and in regard to the rugosity in different degrees of exposed surface (cf. V.B. ¶ 86, 150). Amorphous glassy matrix of "acid-proof" products are preferably dissolved,[79] when the rugosity is high, whereas, the homogeneous glass resists much better. Empirically, one may develop sequences of the oxidic components of "acid-proof" ceramics, with increasing tendencies of dissolution by H_2SO_4, HCeL, and phosphoric acid which are individually different from data for standard specifications prescribing the use of boiling 78% H_2SO_4 solution, for 5, 15, and 30 hours, for glazed ceramic products and true (homogeneous) acid-resistant industrial glass products. Wollast *et al.*, who demonstrated that the conventional assumption that the acid treatment of glass surfaces would leach away only the alkalies, is *not* correct, whereas silica distinctly also goes into solution, and is easily detected and determined by the well-known silica-molybdenum complex method.[80] From the quantitative data of silica dissolution, a typical Langmuir adsorption isotherm can be constructed as a function of H^+ ion activities, for pH below 2.0. The formation of a leached layer on the other hand, is confirmed by the observation of a typical induction period of the dissolution reaction, followed by a constant rate of dissolution over the range of pH from 0 to 2.8. For pH below 0 (negative range) there are other reaction phenomena, and a final stopping for a critical dissolution threshold. Acid anions of the solvent do *not* influence the type of the dissolution reaction; the existence of true protective layers is substantiated also by infrared absorption-spectroscopic data.

[76] *Glass Technol.* **10**, (2), 40–42 (1969).
[77] *Silikattechnik* **21**, (3), 84–86 (1970).
[78] *Verres Refract.* **24**, (6), 251–253 (1970).
[79] Cf. P. Schroth, *Diss. Tech. Hochschule Aachen*, 1959, 36 pp.
[80] Cf. E. Winter, *Glastech. Ber.* **41**, (12), 522–526 (1968).

CONSTITUTIONAL EFFECTS ON THE CHEMICAL DURABILITY OF GLASS

463. We owe to A. Sendt a series of reports on the influence of hydrogen ions on the mechanical strength and chemical durability as a function of the inner constitution of technologically important glasses. In one publication,[81] Sendt refers to the alleged improvement of chemical durability of the glass surface when it is treated with SO_2 gas for the gas atmosphere of annealing lehrs (cf. ¶ 433 f., "sulfuring" effects), which is equivalent to an alkali ion exchange and goes hand-in-hand with improvements in the mechanical stability of glass rods determined by bending strength measurements in air and in vacuum. Sendt emphasizes that besides the well-known reduction of static fatigue after a treatment, and the influence of water vapor, a notable decrease of the T_g (transformation range) is caused by the presence of H^+ ions replacing Na^+ ions in the glass surface as a kind of a "healing" effect. The depth to which the SO_2 improvement reaches is relatively considerable (namely about 10 μ), whereas the surface layer, in which the number of nonbridging oxygen anions is lowered and Si—O—Si bonds are formed by condensation, is very much thinner.

464. The higher mobility of hydroxyl ions in the glass surface and the improved diffusion is thus understandable. The improving effect of the SO_2 gas treatment, technically speaking, is dependent on the influences of mechanical friction, e.g., on the contacts of the glass surface with guiding (metal) rolls which are observed in wide variabilities of the etching behavior of the glass with dilute HF solution. On the other hand, the improvement effect of the ionic exchange $H^+ \rightleftharpoons Na^+$ is higher when the glass surface is less defective. Even for the alkali-free special *E* glass (for glass fiber production), in which the cation exchange concerns the scheme $2H^+ \rightleftharpoons Ca^{2+}$, is responsible for an improvement in the glass substance by a treatment with SO_2. The H^+ and Li^+ ions in the ion-exchange surface also improves the chemical durability, but there is a maximum effect for definite pH values. When Na citrate exerts its strong effect on the reactivity of the glass surface with H^+ ions, a kind of a "neutralization" occurs. Pressure strains in the glass which are often responsible for changes in the chemical durability of (inhomogeneous) glasses do not reach as deep as does the ion exchange and the improving action of SO_2 of about 10 μ (see above).

465. In *mixed alkali* silicate glasses, Sendt[82] measured the self-diffusion of Na^+ and K^+ ions by the radioactive tracer method for ^{24}Na and ^{42}K, as a function of the

[81] *Glastech. Ber.* **37**, (2), 102–115 (1964).
[82] Glastech. Ber. **37**, (2), 116–122 (1964).

ratio Na/K in the glass compositions. With increasing concentration in K^+, the mobility of the Na^+ ions lowers exceedingly rapidly; on the other hand, the diffusion coefficient of K^+ ions is changed only slightly by the simultaneous presence of Na^+. An ion exchange of Li^+ with Na^+ and K^+ mixed alkali glasses show widely differing concentration gradients for one single alkali ion. When Li^+ migrates into a mixed Na–K glass, two different diffusion mechanisms are superimposed on one another, namely the site exchanges $Na^+ \rightleftharpoons Li^+$ and $K^+ \rightleftharpoons Li^+$ which are independent from one another but determined by the self-diffusion coefficient of Na^+ and K^+. In an electric field, the conductivity of a pure alkali silicate glass becomes dependent on the current direction as soon as a foreign cation enters the glass, as is shown by electrolysis experiments with Na–Ca silicate glasses into which K^+ ions are transported by the current, or H^+ ion from a dilute solution of H_2SO_4. When the poles are reversed, very characteristic discontinuities in the current intensity versus time curves are observed.

466. G. Bonetti, B. Locardi, and M. Tornati[83] studied structural anomalies in $Na_2O-Li_2O-Al_2O_3-SiO_2$ glasses of the physical properties (density, fraction index, specific resistance) and of chemical durability in the light of the V. V. Vargin and K. A. Yakovleva[84] theory of improvement effects caused by the introduction of alumina into simpler alkali–Ca silicate layers. The chemical durability does not so much depend as much on the ratios Al^{3+}/R^+ as on the amounts of Li^+ introduced into the glass. The selectivity in the role which is played by Li^+ in the chemism of aluminosilicates here in question, also goes parallel with a pronouncedly higher tendency of the Li^+-containing compositions for devitrification and crystallization.

467. For Na borosilicate glasses in which the ratio of B_2O_3/Na_2O varies between 6.65 and 2.90, Thach Lan Tran[85] studied the phase-separation conditions (cf. Vol. VII.A. ¶ 380, 460) by electron microscopy and replica techniques on fracture surfaces prepared *in vacuo* of a remarkably distinct fine-granular structure, which confirms the formation of finest droplets which not only contain Na borate but silica as well, in agreement with the results of electron-beam microprobe analyses.

468. The chemical durability of Cabal glasses (system $CaO-B_2O_3-Al_2O_3$) and its changes when increasing amounts of boric acid are replaced by silica, were studied by K. Searstone and J. O. Isard[86] using the common grit leaching methods. B_2O_3 is preferably dissolved by pure water, the rate of reaction being determined

[83] *Vetro Silicati* **14**, (1), (49), 9–14 (1965).
[84] *Zh. prikl. Khim.* **34**, (2), 425, 446 f. (1961).
[85] *Verres Refract.* **19**, (6), 416–428 (1965).
[86] *Glass Technol.* **6**, (6), 184–189 (1965).

by a diffusion process through the undissolved aluminum hydroxyde as the residual reaction product on the surface of the grit particles. The correlation between the chemical durability data and the chemical composition of the glass is extremely complex; however, it is noteworthy that glasses high in Al_2O_3 have the highest durability. With increasing amounts of alumina replacing silica, the leaching resistivity is considerably increased; a glass with 10 mole % SiO_2 would have approximately the same, or slightly better, durability than common glasses for bulbs and flasks.

469. A glass of the ternary eutectic composition 20.3 wt. % MgO, 18.3% Al_2O_3, and 61.4 wt. % SiO_2, shows a beginning crystallization temperature of 975°C (measured by differential-thermal analysis); its water-leaching behavior according to S. Kumar[87] is about like that of Pyrex glass. L. Marchesini and G. Scarinci[88] determined the hydrolytic stability of borosilicate glasses by grit leaching, and the changes in this property when alumina was systematically added (from 0 to 7 mole %), with spectrophotometric methods used for determination of SiO_2, Al_2O_3, and B_2O_3—and flame photometry for Na_2O. The addition of even slightly less than 3% alumina is indicated by immediate reduction in miscibility and a stress release and readjustment of surface strains between two liquid phases. At the same time, the structural stabilization effect of alumina is observed in the prompt reduction of leachability and loss of less Na_2O. The electron microscopic examination also indicates a remarkable reduction in the differences of surface tension of the two liquid phases in the unmixing region of the ternary, alumina-free field of the phase diagram.

470. In studying the hydrolytic durability of special glasses for the chemical industry, the laboratory, and pharmaceutical-biological purposes, H. Wessel[89] again touches on the problems of surface improvement by a treatment with SO_2 gas; of protective coatings of silicone and similar methods as recommended by different pharmacopoeiae, and of coating of glass by oxides like SnO_2 by spraying and hydrolysis of $SnCl_4$. References also are given for the conditions and specifications which must be met by gauge glasses, glass tubing, pipelines, and the like. How drastically the properties of common laboratory and instrument glasses can be improved by small amounts of La_2O_3 and of ZrO_2 is made impressive in a report presented by S. K. Dubrovo and A. D. Shnypikov.[90] It is not only the strong Si–O–Zr bonds which bring about favorable physical-chemical properties in general;

[87] *Trans. Ind. Ceram. Soc.* **25**, (4), 85–92 (1966).
[88] *Vetro Silicati* **11**, (2), (62), 5–11 (1967).
[89] *Silikattechnik* **18**, (7), 205–211 (1967); **19**, (1), 6–10 (1968).
[90] Proc. Conf. Silicate Ind., 9th, Budapest, 1967, pp. 459–466, Akadémiai Kiadó, Budapest, 1968.

the hydrolytic and alkali resistance of Zr silicate glasses exerts a positive effect. Although the bond strengths of La^{3+} cations are by far weaker than those of Zr^{4+}, the introduction of La^{3+} in a moderate amount does not influence the chemical durability very much; a complete replacement of Zr by La would cause a relatively strong "depolymerization" effect, an important increase in the thermal expansion coefficient, a much lower softening temperature, and higher weight losses by alkaline solution reactions of glasses with such a modified glass composition.

471. It is instructive to compare the last-mentioned observations with the changes in Na – Ca silicate glasses when silica is partially replaced by TiO_2, CeO_2, and $AlPO_4$ as was done experimentally by Tr. Bååk, C. F. Rapp, H. T. Harley, and B. E. Wiens.[91] The chemical resistance was determined from glass grit, with hydrolytic and acidic leaching methods (using 0.02 *N* H_2SO_4, and 5% NaOH solutions). A substitution of silica by GeO_2 barely changes the reactions, whereas for TiO_2 and $AlPO_4$, there is up to 0.5 mole % of the additions, some reduction of hydrolytic resistance; above 0.5% there is an increasing tendency. Most striking is the improvement in chemical durability of ZrO_2 when this replaces silica, and the increase in resistivity to alkaline solutions; but more than 2% GeO_2 acts in the opposite direction.

472. Problems of the production of refractory glass fibers (cf. VII.A. ¶ 574 ff.) are illustrated by L. E. Gates and W. E. Lent,[92] starting with the system $SiO_2 - Al_2O_3$ but with systematic variations in the content of MgO, ZnO, PbO, ZrO_2, Ce_2O_3, Y_2O_3, V_2O_5, and CaF_2, as a fluxing agent for acceleration of glass fusion, e.g., in the electric arc furnace from which the fibers are spun, or in an acetylene plus oxygen flame with a service temperature which could be driven higher than 1800°C by dipping Wo electrodes into the batch. Again, the best results were achieved in systems of silica-alumina with additions of MgO, ZrO_2, and P_2O_5, whereas the systems $BaO - Al_2O_3$ and $CaO - Al_2O_3$ with large additions of ZrO_2 had a great tendency to crystallize from the melts. An electric arc-heated spinning device proved to be a very efficient tool for a continuous fiber production.

473. Moderately refractory, but *porous*, glass fibers on the basis of silica (up to 98%) were prepared by A. I. Khomutov, A. F. Zak, and G. S. Popova[93] by an acid-leaching reaction for a full reproducibility of low-porosity characteristics. The best among those "silica" glass fibers are recommended for adsorption beds in drying, separation, and contamination–elimination processes in chemical technology. Very similar results in glass fiber production methods were obtained by

[91] *Bull. Amer. Ceram. Soc.* **47**, (8), 727–730 (1968).
[92] *Bull. Amer. Ceram. Soc.* **46**, (2), 202–205 (1967).
[93] *Zh. Prikl. Khim.* **42**, (6), 1279–1285 (1969).

M. A. Matveev and V. M. Solodukho[94] (cf. ¶ 311, 327, 342, 459) in continuous fiber drawing machines. Interesting data of microhardness measurements of such products containing alumina, magnesia, lime, and titania were also presented to show that TiO_2 increases the mechanical strength values.

474. The production of Vycor glass and other porous glass types were again studied by K. Kawasaki and N. Hackerman[95] who emphasized that by water adsorption such glasses evolve a considerably increased surface conductivity, in different separate steps, namely, a range in which a logarithmic correlation is followed, and a later range characterized by a linear function. The hypothesis of a stepwise approximation to liquidlike states, however, raises questions.

475. C. R. Das[96] studied the hydrolysis of glasses of the system $Na_2O-SiO-TiO_2$ (for 0 to 15% TiO_2, replacing SiO_2) the rate of progressive corrosion being in the first state a function of the square root of time, later of time itself. Also, the diffusion coefficient and the activation energy of diffusion in those reactions could be determined from measurements of conductance. Das reached these conclusions from the high polarization action of the Ti^{4+} cation and its high field strength which induces a copolymerization of the hydroxides and the precipitation of silica hydrogel layers which bring about the reduction in diffusion efficiency.

476. J. Gronau, G. Hilbig, and Kl. Grunauer[97] studied again the cation leaching process in Vycor glasses in several technological details, e.g., the difficulties arising when volume shrinkage or swelling reactions occur during leaching of the B_2O_3-enriched glass matrix of the primary products. Temperature and time conditions have strong influence on the treatments in the range of visible opalescence (580° to 600°C). Therefore, particular care was given to the depths to which the leaching solution penetrates into the glass surface, also for a calculation of a nonlinear differential equation (of first order) for the maximum depth and time which, however, will not be reached in the practical operation conditions. The diffusion coefficient increases with increasing reaction time. Adsorption isotherms for water on the surface of the leached porous glass were used for a graphic determination of the pore volumes distribution curve from which one may see how the specific surfaces decrease with increasing time periods of thermal treatment (cf. Vol. V.B. ¶ 212–215). The diameters of the pores increase in the same process.

477. An essentially new development is a chromium tripolyphosphate glass which, according to presumptions of D. Betteridge and G. N. Stradling,[98] may be

[94] *Silikattechnik* **19**, (6), 181–183 (1968).
[95] *Surface Sci.* **10**, (2), 299–302 (1968).
[96] *Ind. Ceram.* **13**, (1), 30–41 (1968).
[97] *Silikattechnik* **21**, (6), 189–191 (1970).
[98] *J. Inorgan. Nucl. Chem.* **22**, (10) 2652–2654 (1967).

used in chemical technology as an excellent ion-exchanging substratum for alkali metal ions. The high importance of modern ion-exchange reactions for a multiple solution of problems in glass strengthening (cf. Vol. VII. ¶ 899–902) as seen in a series of special publications (eight) A. J. Burggraaf, may be here only briefly mentioned to demonstrate advances made in research into cation-exchange reactions alkali alumino-silicate glasses, in connection with structural changes in the glass, and the mathematic description of stress relaxation after the cation exchange.

EFFECTS OF ORGANIC AGENTS; CHELATING REACTIVITY

478. It is feasible to recall other investigations of the corrosion action of *organic* compounds in aqueous solutions on glass surfaces of which we, in recent years, are accustomed to speak as of *chelating* effects. We do not want to repeat what has been discussed in the Vol. VII. ¶ 643, 648 on the specific adsorption of quaternary ammonium halides in aqueous solutions onto glass as described by J. Kivel, Fr. C. Albers, R. E. Johnson, and D. A. Olsen,[100] but it is advisable to think of similar phenomena in connection with the stability of antique silicate glasses such as glazes on antique ceramics which did either withstand, or yield, to corrosion by the action of organic amines and amino acids. We do not wish to omit phenomena which play a part in the interpretation of changes that have taken place in fragments of glazes on antique ceramics from Greek, Roman, or even much older civilizations. Chemical-analytical and microanalytical methods are of great value and conclusiveness here; also electron microscopic examinations are indispensable, and we cite as excellent examples, studies by Fr. Oberlies and N. Köppen[101] of Greek vase ceramics of great beauty, in an excellent state of preservation.

479. Of very similar type are the microstructures of lead–manganese–copper aluminosilicates in majolica luster glazes, matured in an oxidizing atmosphere, as described by C. R. Beechan and W. O. Williamson.[102] The luster was studied in the polarization microscope as an orientation effect of crystallization during cooling of the glaze, which as was confirmed also by X-ray diffusion analysis in the glassy matrix of such ceramic bodies is highly variable in composition. This is clearly observed by changing the contents of heavy metals which bring about the "bronzy" or "gun-metal" luster effects.

480. Another observation of detrimental corrosion effects of organic origin

[99] *Phys. Chem. Glasses* **7**, (5), 169–172 (1966); **7**, (5), 173–177 (1966), with W. J. Spoor.
[100] *J. Phys. Chem.* **67**, (6), 1235–1238 (1963).
[101] *Ber. Deut. Keram. Ges.* **39**, (1), 19–31 (1962).
[102] *Trans. Brit. Ceram. Soc.* **62**, (11), 939–948 (1963).

revealed the defects caused by mushrooms and fungus growth on the surface of optical glass, chiefly on highly polished lenses or mirrors. This extremely troublesome phenomenon was studied by G. Theden and W. Kerner-Gang[103] in searching to develop new standard test specifications for the protection of optical glass instruments. Xerophilic, mesophilic, and hygrophilic lichens and mycel-forming fungi equally etch optical glass; spores may germinate and grow without any direct afflux of nutriments which might come from foreign sources as fouling fungi in moist-chamber conditions. The chemical nature of the glasses in question is of particular importance for rapidly growing (tonophilic) aspergillus, at surprisingly low partial pressures of water. A rich collection of micrographs of such defects caused by fungus on optical glass is given by the same authors.[104]

481. Doubtlessly neglected, but of great importance for city hygienics and for waste valuation, are proposals and experimental observations made by E. Spohn, E. Woermann, and D. Knöfel,[105] which disclose the perhaps surprising fact that when glass cullet with sharp-angular and cutting fragments is embedded in, or for some time exposed to, reaction with agricultural compost, it loses its sharp edges rather soon, due to such organic agents as lichens, mycorrhizae, fungi, and other vegetal organisms, by chelation of organometallic compounds. Microbacteria of lithobiontes behave particularly modellike in the laboratory experiments with fragments of volcanic glass. Additional experiments showed a depth effect of about 25 μ in such etching reactions, which is particularly intense along scratches on the glass surface.

482. M. Prod'homme[106] examined the bacterial decomposition of a potassium aluminophosphate glass,[107] doped with ^{32}P and exposed in Petri dishes to *E. coli* bacteria for 48 hours. The contact zone between the glass and the culture gelatin showed a radioactivity after exposure of 5000 impacts/minute; therefore also, assimilation of ^{32}P into bacteria cells from the substance of the glass takes place.

INFLUENCE OF CORDS ON HETEROGENETICS IN GLASS ON DURABILITY

483. The kinetics of leaching lead from a silicate glass by ethylene diamine tetraacetic acid (EDTA) was analyzed in detail by D. A. Olsen, R. E. Johnson,

[103] *Glastech. Ber.* **37**, (4), 200–205 (1964).
[104] *Glastech. Ber.* **37**, (5), 256–259 (1964).
[105] *Stadthygiene*, 1965(6) reprint.
[106] *Verres Refract* **22**, (2) 170 (1966).
[107] Cf. B. E. Moody and D. G. Monk, *J. Soc. Glass Technol.* **42**, 88T–100T (1958).
[108] *J. Amer. Ceram. Soc.* **52**, (6), 318–322 (1969) (cf. VII. ¶ 648 f.)

J. Kivel, and Fr. C. Albers.[108] A lead-containing alkali silicate glass proved to be particularly notable for a two-step reaction involving hydroxyl ions with the chelating agent. Beyond the leaching of Pb^{2+} in a stable solution complex, K^+ and Si^{4+} ions are mobilized, but no complexes formed with EDTA could be identified. The removal of Pb^{2+} most probably loosens the structure of the glass surface, thus making the leaching of K^+ and Si^{4+} easier in the second step. Later, the chelated silica is again precipitated to form a layer of silica hydrogel on the glass surface which, by chelating-etching and gel formation, reaches a higher degree of rugosity which is visible in replica-electron micrographs. These effects could also be confirmed by interferometric measurements analogous to those made by D. A. Olsen, R. E. Johnson, and K. H. Olsen,[109] of similar silica hydrogel layers on the etched lead silicate glass which is highly vulnerable to hydroxyl attack combined with that of EDTA.

484. Such combinations of interferometry and etching are characteristic of more recent investigations made by J. Löffler, in his classical studies of surface layers and striae (cords) in glass cross sections (cf. Vol. II.B. ¶ 187, 193). This author wrote a report[110] and a fascinating article[111] on the development of characteristic profiles of cords and striae caused by heterogeneities in the first treatment of apparently homogeneous massive glass. A differential etching method using dilute acids (HCl, HF) and NH_4F + HCl results in an etch surface that proves to be "sculptured." By differences in the light refraction properties of the matrix glass, and the individual cords and layers (in profile), the interferometric method makes possible a reliable interpretation of the discontinuities in composition and density of the single layers.

485. A half-quantitative method could be worked out which would be highly significant for all studies of homogenization for the current control of sheet and plate glass during manufacturing and for detecting variations in the amount of limestone and dolomite in the glass batches, or defects caused by incomplete mixing effects or residual assimilation of sand (dissolved quartz), assimilation residues of silica and alumina from refractory material like the Corhart (standard), and fireclay refractories from the walls of the glass tank, and many more details. The accuracy of interferometric methods is of high value when strictly monochromatic light is applied (nonfiltered Cd light may be sufficient when a rapid orientation is desirable). Impressive examples are given by Löffler. For a desirably high accuracy of the

[109] *Glass Technol.* **11**, (4), 119–122 (1970).

[110] See also *Glastech. Ber.* **37**, (12), 548–553 (1964).

[111] Cf. Vol. IV. Part 4, of the section "Microscopy in Glass and Enamel Technology" in the "Handbuch der Mikroskopie in der Technik", by H. Freund, Umschau-Verlag, Frankfurt/Main, 1964.

measurements, the use of the Sabatier effect (construction of equidistant curves) is recommended.[112]

486. More practical aspects are formed in another report by J. Löffler[113] on determination of the degree of homogeneity of glass production, with examples of glass plant surveys[114] and the use of H. Schardin's "cord microscope."[115]

487. Other contributions by Christ.a.J. Löffler[116] concern the use of the electron-beam microprobe for the determination of alumina in cords. In comparison with common wet-analytical methods, the microprobe techniques are superior by making possible examination of quite localized areas of a glass surface, and to distinguish the composition from that of the surrounding glass matrix. A technical improvement is the creation of a conductant layer of Be metal, vacuum-sprayed onto the glass. Another important practical experience of Löffler's is that the alkali silicate distribution in cords is coupled with assimilation reactions with refractories of glass tank walls (mostly Corhart standard or firebrick material) and related problems. Analbite and nepheline are typical mineralizations in such reaction glass cords; surprisingly enough, mullite is very scarcely observed in such zones.[117] The same authors[118] illustrated the application of the electron-beam microprobe on samples with critical fields only 2.5 μ in diameter for a detailed chemical analysis of typical glass cords.

488. Typical alumina-enriched cords in flat glass, and their diffusion profiles for SiO_2 and Al_2O_3, were described and measured by H. Becker[119] on plane contacts by using Löffler's interferometric methods which proved to be very sensitive for this purpose. In other cases, even common refractometric measurements were sufficient evidence that for control of glass homogenization, the diffusion effects of silica and alumina are needed, but that those of alkalies and alkaline earths are not essential. In contrast with the data for self-diffusion of alumina, those for silica showed a very close agreement in both the diffusion analysis in concentration striae and with the self-diffusion coefficient. The self-diffusion of alumina (^{26}Al) is by one order of magnitude higher than is the diffusion of alumina in the cords.

[112] See E. Lau and W. Krug, "Aequidensitometrie", Akademie–Verlag, Berlin, 1957.

[113] *Verres Refract.* **19**, (4/5), 259–268 (1965).

[114] As a Report to Subcommission III, Commission Internationale du Verre, translated into German, in *Glastech. Ber.* **38**, (4), 269–276 (1965).

[115] Reference 114, described in *Glastech. Ber.* **27**, (3) 70–79 (1954).

[116] *Glastech. Ber.* **39**, (4), 333–334 (1966).

[117] Cf. V. B. ¶ 113; 117, footnote 384; see also K. T. Bondarev, V. A. Minakov, and A. A. Zaĭkina, *Izv. Akad. Nauk S.S.S.R., Neorgan. Mater.* **1**, 883–887, (1965) with extensive analytical data of zones of chemical uniformity of dimensions in the range from 30 to 100 μ, and the distribution of SiO_2, CaO, Al_2O_3.

[118] *Steklo Keram.* **22**, (7/8) 514–516 (1965), (Engl. transl.).

[119] *Glastech. Ber.* **39**, (12), 519–524 (1966).

489. H. Becker[120] also discussed the influence of the glass flow on homogenization in sheet glass tanks, with the evolution of typical layer patterns (cf. Vol. II.B. ¶ 71 ff.). The macroscopic and microscopic examination of sheet glass cords make evident the prevailing character of the drawing-out of cords to thinnest layers as many factors which are influencing and even rule by dimensional conditions of the tank reservoir and the glass bath, but also by boundary face tension forces and the breaking (or complete inhibition) effects which they can exert on the striae layer evolution. It makes a great difference whether or not the drawn-out striae have been undistorted before the glass ribbon is shaped, or if they were deformed in the flow, forming wedgelike faultings, which are easily visible in cross sections through the ribbon. Finally, the hot spot region in the tank melt may play an important role in the homogenization process and mechanisms (cf. ¶ 106ff., 176.).

On the use of the electron microprobe and the X-ray microanalyzer in the control of glass homogeneity, we also briefly cite an illustrative contribution and observations by R. V. Adams, H. Rawson, D. G. Fisher, and P. Worthington.[121]

490. J. Coenen[122] studied the important technical question of whether the density of cord glasses may influence the flow characteristic and the way of the glass in the bath of a tank furnace, i.e., whether ascendent and descendent currents in the bath may influence buoyancy effects or the fluctuation program of the melts. This problem cannot be solved by simple calculations based on density measurements of the surrounding matrix glass in comparison to that of the bulk, even when the composition most closely approximates the final assimilation products which, to a great portion, make up the substance of the cords. Coenen, nevertheless, contributed details of considerable value by investigations based on the quaternary system $Na_2O-CaO-Al_2O_3-SiO_2$ and different types of arbitrarily chosen reaction glass melts of well-defined position in their representative point sites in the quarternary phase diagram, over the temperature range from 800° to 1450°C and combined with determination of *relative* densities (Fig. 116). The chosen compositions are focusing along the valley between the fields of primary crystallization of cristobalite and albite which, at high temperatures, show a very distinct maximum of specific volume, but of lower densities than are to be expected for the surrounding glass and, therefore, creating a tendency of the model "cords" to flow upward.

491. Reaction products of the Na–Ca silicate glass melts with the material of highly alumina-enriched refractories (Corhart type), however, must show the opposite tendency to flow downward when loaded with Al_2O_3. When a nepheline-type eutectic melt reacts with the matrix glass, more highly complex phenomena

[120] *Glastech. Ber.* **40**, (4), 124–126 (1967).
[121] *Glass Technol.* **7**, (3), 98–105 (1966); cf. ¶ 171.
[122] *Glastech. Ber.* **39**, (3), 81–89 (1966).

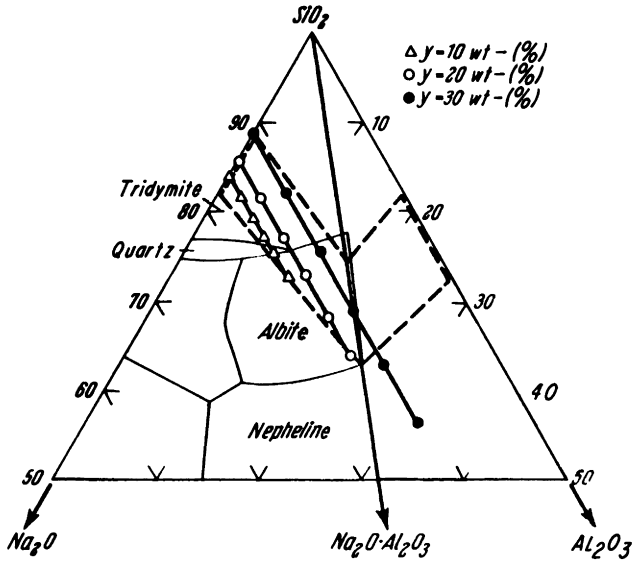


FIG. 116. Phase equilibrium diagram of the ternary system $Na_2O-Al_2O_3-SiO_2$ with indication of glass melts of the composition type of experimental glass ("l"), with addition of y wt. % of a mixture $qSiO_2$ and $(1 - q)Al_2O_3$. (Coenen.)

may occur which cannot be directly predicted. Coenen carefully considered the influence of the different coordination of the Al^{3+} with O^{2-} anions to be expected in the assimilation glass products ("cords") in which the coordination $[AlO_4]$ will prevail, whereas the $[AlO_6]$ coordination indicates a possible crystallization of corundum or mullite, and thus to favor the formation of a reaction glass of higher density. The investigations of Coenen show, in every case, how misleading and uncertain it must be to try to use density data measured at room temperature for extrapolations of the behavior of the glass in the bank melts. Coenen's discussions also give a very convincing interpretation of the influence that B_2O_3 must have on many industrial glasses and on the reactivity of the cords with refractories of the furnace lining. B_2O_3 evidently favors the changes in coordination of Al^{3+} in the cord-infected glass portions. Diagrams like that in Fig. 117 present a first orientation of the fundamental conditions ruling the density factors and their effects.

492. T. W. Brock and D. L. Carter[123] gave representative indications for a well-based *physical* classification of the nature and properties of glass cords which may

[123] *Bull. Amer. Ceram. Soc.* **45**, (6), 574–577 (1966).

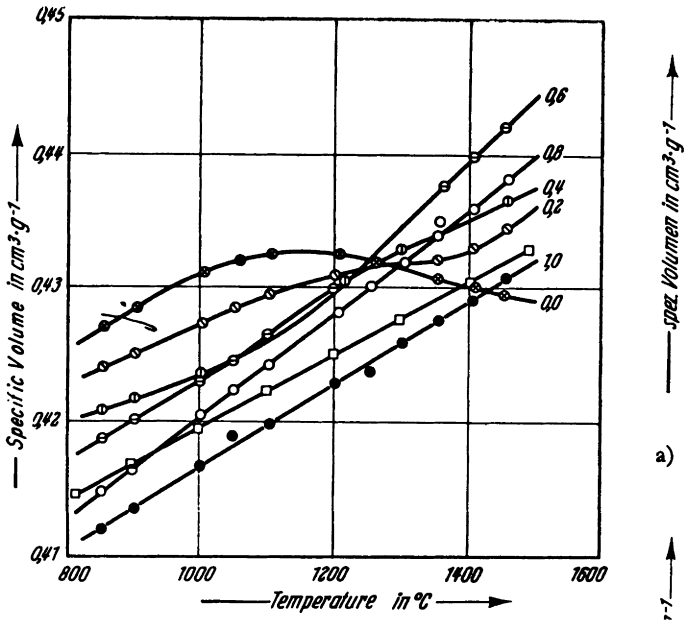


FIG. 117. Specific volumes as a function of temperature for glass melts of the same variable glass composition, but with $y = 20\%$. (Coenen.)

normally occur in glass manufacturing. They used measurement data of residual strains in the cords, determined by the etching test method of J. Löffler (cf. Vol. II.B. ¶ 187), and data of refractive indices, according to J. Francel and J. S. Longuidice,[124] supplemented by a flow chart of cord analyses for a simple Na–Ca silicate glass. One may also use standard data from a suitably chosen glass sample with "synthetic cords" of defined composition which may refer to systematic contents in silica, alumina, zirconia, and may be adapted from case to case to varied practical experience and requirements.

493. The X-ray fluorescence analysis method offers many most welcome new and practical possibilities for an identification and half to full-quantitative determination of cord compositions in glass, as R. J. Quentin and Fr. H. Boone[125] demonstrated. They suggest that separation of striae material in grain fractions from the matrix glass is best done by the classical immersion method in heavy liquids of accurately known densities, followed by the normal centrifugation into density

[124] Cf. Symp. on Glass Melting, Union Sci. Continent. du Verre, Charleroi, 1959, pp. 771–790.
[125] *Glass Ind.* **48**, (10), 538–539 (1967).

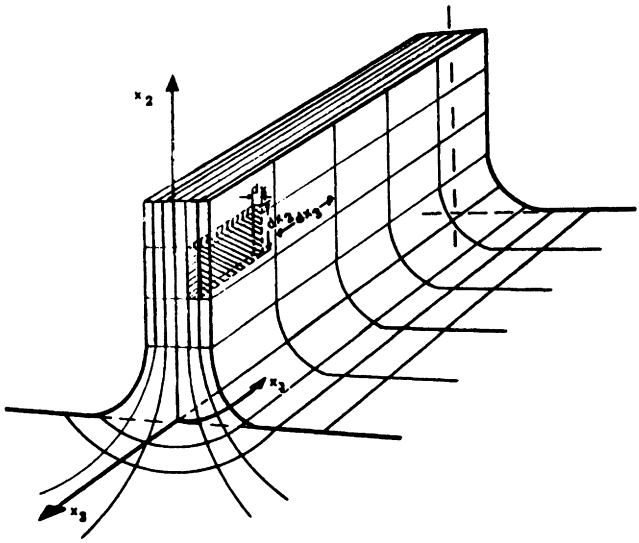


FIG. 118. Volume element dV in a glass lamella drawn from the glass melt. (Tribuno and Tettamanzi.)

fractions, then emission spectroscopy and X-ray fluorescence analysis. The authors show examples taken from plant practice for container, sheet, and flint glasses.

494. For classification problems of glass cords, C. Tribuno and N. Tettamanzi[126] gave interesting new suggestions starting from their "dynamothermal" evolution in glass fusion of so-called "physcial" cords for which the viscosity–temperature curves give the rheological premises of their origin in chemically homogeneous ("pure") glasses. The cords from complex laminary systems (Fig. 118) illustrate the well-known example of lamination in the Fourcault glass machine process, best studied in glasses which had undergone drawing, pressing, or rolling. Such "physical" cords may disappear again when subjected to a planned thermal treatment after having reached a certain degree of viscous mobility; Tribuno and Tettamanzi suggested that such cords might occur as typical "physical" cords in silica glass. Of course, for an understanding of this definition, it must be emphasized that in contrast with "physical", "chemical" cords follow basically different rules of examination, classification, and homogenization treatments than those discussed by the authors.

495. A qualitative spectrographic determination of the composition of cord glasses was recommended by Zd. Haberman,[127] based on the principle of selective volatilization of elements in an alternate current plasma, using the Zeiss Q 24

[126] *Verres Refract.* **21**, (4), 289–294 (1967).

[127] Veda a Vyzkum v Przumyslu Sklarskem **10**, 113–122 (1967).

medium dispersion quartz spectrograph (generator ABR 3) from a graphite substratum electrode (slit resolution 0.01 mm), with a sufficient separation for the distinction between matrix and cord glasses.

496. A. Sevin and J. Daudans[128] used similar arrangements for the identification of such crystalline inclusions in glass residues from Corhart assimilation in glass melts, secondary corundum, zirconia (primary and secondary), quartz, devitrite, tridymite, and the like (cf. Vol. II.B. ¶ 207; Vol. V.B. ¶ 113). Emphasis is given to local conditions of assimilation that depend on differences in construction details of the glass tanks. In this respect, we may recall the repeatedly cited observations made by J. P. Hazart and E. Weinryb[129] with the electron-beam microprobe.

497. Streaks in glass may become valuable in production control when in glass furnace fusion and fining they disclose details of viscous flow during temperature decreases, or of the introduction of foreign, often submicroscopic, particles. They may show in the machining and final shape-giving when all material fluctuations are frozen-in. That recording regular striae diagrams gives the surveying engineer much information in control and information during the manufacturing process was demonstrated by N. Tettamanzi and N. Villa.[130]

498. Once again, the electron-beam microprobe, according to J. P. Hazart,[131] has been from the beginning an excellent tool for the detection of glass defects by the speed with which it gives information, with semiquantitative orienting indications, e.g., in "profiles," clear-reading micrographs, and even reliable quantitative determination of elements in glass composition on smallest fields (1 μ^2) or inclusions (cf. II.B. ¶ 203 ff.).

499. J. Daudans, A. Krings, and A. Sevin[132] gave particularly significant evidence that the superstructure of glass furnaces is the source of many typical glass defects. Specific corrosion reactions of the glass with refractories in the roof (on devitrification phenomena of this kind, cf. ¶ 530) in this portion of the furnace make notable contributions of material from batch dust and so-called "nepheline worms" in drops or glazes in sheet glass tanks. Again, the electron-beam microprobe was very helpful in identification and analytical control of purely vitreous reaction products. Nepheline "worms" are observed settling to the bottom of the tank, then migrating to the gathering ends; they are particularly dangerous to the continuous glass production because of their persistence in the range of relatively low temperatures in the bottom glass ("sludge").

[128] *Glass Technol.* **8**, (4), 103–107 (1967).
[129] *Verres Refract.* **22**, (2), 145–162 (1968); cf. II.B. ¶ 71, 75; this volume, ¶ 74; 386.
[130] *Vetro Silicati* **12**, (3), (69), 16–19 (1968).
[131] *Silicates Ind.* **34**, (10), 269–276 (1969).
[132] *Glastech. Ber.* **42**, (10), 392–395 (1969).

DETERIORATION OF OPTICAL AND RELATED SPECIAL GLASSES BY MOISTURE

500. An extensive special report on the surface deterioration phenomena of optical glasses was presented by K. Kinoshita[133] with practical observations of typical changes in the texture of the glass surface,[134] in comparison with the behavior of Pyrex, Vycor, and common plate glasses, and measurements of changes in the refractive indices. The growth of crystallites on the glass surface was also described in characteristic examples. Of particular interest, however, is the formation of a layer (called "aoyake" = blue skin) in which, by leaching, more or less irregular changes in the optical properties are observed, often recognized by interference phenomena, e.g., vivid colors playing in reflected light. On this basis, Kinoshita developed a detailed mathematical discussion of the heterogeneities in the optical properties, including swelling and shrinkage phenomena in colloid films, adsorption reactions, aging effects, and the like. Most instructive are Kinoshita's recommendations for the detection of early stages of the "aoyake" evolution, and of its influence on antireflection coatings (cf. ¶ 285); an imperceptibly thin aoyake of a thickness of less than 10 μ can show itself as vividly colored patches when coated. Related phenomena are the well-known "breath (haze) patterns."

501. The presence of breath patterns as the consequence of moisture effects on the stability of optical glass, are in a certain respect similar to the behavior of expansion effects in structural ceramics (cf. Vol. V.B. ¶ 13) for which we give a brief reference to an article by I. L. Freeman and R. G. Smith,[135] and to the behavior of porous glass as studied by M. J. D. Low and R. Ramasubramanian[136] (cf. Vol. VI.C. ¶ 256; Vol. VII. ¶ 647, 946). We also cite optical glass studies by H. Wessel and Chr. Heindorf[137] on a recently modified test of particularly stain-sensitive glass types which require a careful application of protective films. The interference microscope[138] was also used by Irina Zberea[139] for studies on "microreliefs".[140]

502. The most detrimental, but often too late recognized, damage to optical glass, is the effect of *air moisture*, and we have every reason to take seriously the

[133] In "Progress in Optics" (E. Wolf, ed.), IV, pp. 87–143, North-Holland, Amsterdam, 1965.

[134] See also Kinoshita's investigations on the surface of polished glass, using the ellipsometric method in *J. Appl. Phys. Jap.* **3**, (13), 805–808 (1964); cf. Vol. II.B. ¶ 181, 188, including also optical glass.

[135] *Trans. Brit. Ceram. Soc.* **66**, (1), 13–35 (1967).

[136] *J. Phys. Chem.* **71**, (3), 730–737 (1967).

[137] *Silikattechnik* **18**, (2), 42–45 (1967).

[138] Cf. S. Tolansky's method, "Multiple Beam Interferometry of Surfaces and Films," London, 1948.

[139] *Rev. Roum. Sci. Tech., Ser. Met.* **12**, 1967 (1) 41–49.

[140] Cf. S. Tolansky in "Surface Microtopography," London, 1960.

experience of J. Löffler in glass technology.[141] Löffler sees the specifically obnoxious action of even small local traces of moisture on their boundaries with the glass surfaces which attract water from the surrounding atmosphere continuously until a certain equilibrium is reached between the hydrolysis products, among which NaOH is particularly reactive and reaches relatively high percentages (NaOH equivalents up to 40%) as determined by electrometric titration with HBF_3OH in anhydrous methyl alcohol.[142] In time, silica dissolved in the adsorption surface layer also shows systematically increasing concentrations, e.g., up to 3.75 moles SiO_2 per 1 mole R_2O. Löffler extended his observations and conclusions from silicate glasses also to phosphates which are increasing in "popularity" for modern optical glasses. In several respects, we may compare Löffler's ideas and considerations with the silicate to borosilicate glasses which were specifically studied by M. B. Volf[143] to explain the formation of "scalings" (cf. ¶ 460) as characteristic of changes during the autoclave sterilization in medical laboratory practice.[144]

503. A very particular kind of surface change observed in plate glass and caused by a treatment with SO_2 + oxygen was described by P. Ehrmann, M. de Billy, and J. Zarzycki[145] in which the ion exchange of H^+ from the etching agent (namely, NH_4HSO_4) and Na^+ from the glass surface is a typical dealkalinization (at about 350°C.; cf. ¶ 224 ff.). A white layer of Na_2SO_4 is visually detected as a coating on the surface which is, however, "improved" by the dealkalinization effect, and relatively enriched in silica (dehydroxylized at about 600°C). The appearance of single white spots (about 20 to 80 per cm^2) indicates localized centers of H^+ migration into the glass surface, identified as holes of hemispherical shape, and slightly concave in the meniscus, as seen in the microscopic Fig. 119. Cracks start from such points and develop a characteristic star-shaped pattern, preferably on the surface layer of only 0.1 μ in thickness, but at greater depths show a transition to punctuated patterns in which the migration of H^+ apparently is stopped; the H^+ then must enter the deeper glass layers by diffusion alone, as can be systematically observed by a series of micrographs for the temperatures increasing from 550° to 620°C.

[141] *Glastech. Ber.* **41**, (12), 506–512 (1968); compare L. Holland, "Properties of Glass Surfaces," London, Chapman & Hall, 1964.

[142] Cf. E. Eberius, in "Wasserbestimmung mit Karl Fischer Lösung," Verlag Chemie, Weinheim, 1954.

[143] *Silikattechnik* **20**, (5), 155–158 (1969), at 120°C.

[144] See also P. N. Homer and B. J. Crawford's investigations on microstructures of etched glass furfaces, *Glass Technol.* **11**, (1), 10–14 (1970); cf. VII. ¶ 935.

[145] *Verres Refract.* **18**, (3), 169–180 (1964).

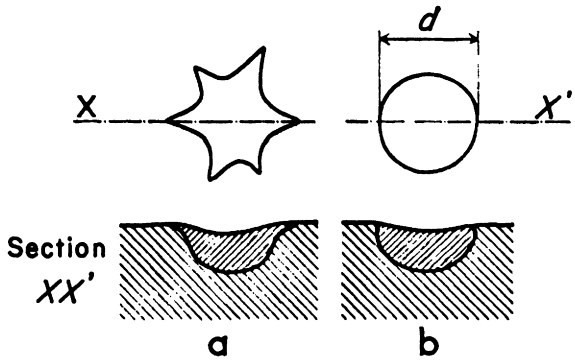


FIG. 119. Schematic representation of hemispherical grooves obtained in glass by (a) corrosive dealkalinization at 580°C (star-shaped grooves), or (b) the dealkalinization at 620°C (bevelled hemispherical shape grooves. (Ehrmann, de Billy, and Zarzycki.)

504. We owe to L. and M. Prod'homme a great many fascinating results of careful microscopic studies. We may cite a few particularly interesting items: M. Prod'homme and Mlle. G. Pigeat[146] found the interference microscopic method to be a particularly successful tool for glass surface techniques (cf. Vol. VI.C. ¶ 33), in combination with a replica technique. In polishing to a high degree of optical quality there are quite specific texture changes which were studied in detail by L. Prod'homme and R. Prat,[147] with refined microscopic methods. The etching of a highly polished surface of different optical glasses with dilute Na_2CO_3 solutions was the subject of other investigations by M. Prod'homme and M. Brochet,[148] at slightly increased temperatures of the etchant solutions from 50° to 90°C using the contrast interference microscope. The results show the influence of different methods of polishing among which the pitch-polished surfaces had the highest resistivity and a distinct "induction period" followed by a transient accelerated material loss, and then a constant abrasion pattern. Of distinct influence are residual hydrogen layers exerting a protective effect and a multiple behavior of diminished transparence of the glass surface during etching which develops fine-granular details in the surface texture.

505. A most instructive report presented by V. A. Ryabov[149] illustrates the

[146] *Silicates Ind.* **29**, (3), 89–96 (1964).

[147] *Verres Refract.* **19**, (1), 22–31 (1965).

[148] *Verres Refract.* **19**, (2), 113–124 (1965).

[149] *Glass Technol.* **9**, (4), 105–112 (1968); with 51 highly valuable references mostly from the Russian literature bibliography.

present state of our knowledge and investigation planning in the wide fields of surface properties of glasses and their influence on the physical and chemical responses of glasses to numerous technological problems and methods. The problems of improvement are, by no means solely the removal of defects (faults) in the glass "skin," which one may simply remove by etching. There are also those to be challenged with a planned combination of artificially applied coating layers which have properties of their own, which, however, may cooperate with those of the glass surface, to effect better "improvement" in methodological measures. For the elementary process of removing faults and surface defects, Ryabov developed a special chemical "glass toughening" apparatus in which even serious surface defects are eliminated with a high degree of safety. In a second step, a protective layer ("skin") is applied by spraying. Silicones are preferably recommended for this purpose.

506. The much undesired frequencies of breakage on shipping could be, as a matter of fact, reduced to a tolerably low frequency. This success is of particular importance for the stabilization of silver (mirror) plate glass, either by a simple dipping in adequate silicone solutions, or even better for nonsilicate surfaces, by a finish with protective layers from an aerosol spray on the glass. We cannot illustrate details of such manipulations here but do emphasize the high degree of quality achieved in the products; we also briefly indicate how successfully the classical silvering methods have been supplemented with thin cobalt foils (on the metallizing of glasses by passing the glass through a layer of the molten metal on a rotating drum; cf. Vol. VII. ¶ 639, 884, footnote 183).

507. Thinnest glass films with well-defined surface qualities were produced by S. Tanaka and D. H. Warrington[150] when pressure blown (2 atm overpressure) especially for the purposes of electron microscopy (thickness of the films about 300 Å). Such glasses must commonly be high in Na_2O (ca. 25%) and bear on the original surface a layer of Na_2SO_4 (hexagonal modification I as identified by electron diffraction analysis) which, however, is decomposed by a more intense irradiation to form an amorphous residue. Tiny spheres of Na metal in a higher state of dispersion were observed in such samples on both sides of the glass film evidently having undergone a temperature increase up to more than 300°C. It is interesting that such glass films for electron microscopy (transmission) purposes can also be produced, according to A. Turkalo,[151] as scalings (splinters) produced from the surface of freshly broken massive glass (cf. Vol. VI.C. ¶193, 198).

[150] *Phys. Chem. Glasses* **5**, (3), 87–89 (1964).

[151] *J. Amer. Ceram. Soc.* **51**, (8), 470–471 (1968).

CHEMICAL DURABILITY OF ENAMELS, FRITS, AND GLAZES IN COMPARISON WITH ANALOGOUS GLASSES

508. Only a very brief comparison may be made here between the chemical durability and the weathering characteristics of representative glassy (vitreous) products more specifically called "glasses", in the strictest sense, and those characteristics of "enamels" and glazes on metal sheets and ceramic substrata.

509. H. J. Oel and A. Dietzel[152] distinguished enamels between *weathering*, as an action of water vapor in the atmosphere, and *leaching*, with liquid solutions as the aggressive agents. In this understanding, results of the weathering method developed earlier by J. Löffler[153] may be ambiguous because unavoidable leaching effects are superimposed on the analytical examination in which alkalies are dissolved from the residues. Leaching is intermingling with the weathering test, when the weathering residues are rinsed and filtered. Oel and Dietzel, therefore, recommend an *optical* method, in the place of a strict chemical analytical examination, for measuring of the time period required for a *visible* weathering layer to develop, or better, until the so-called "glossmeter" device confirms the qualitative visual observation. Majolica enamels show, in a comparison with an examination using the common grit methods, considerably larger leaching effects than when window glass is tested, whereas the weathering shows just the reverse effect. Final pH values, as a function of time, determined with a completely automatic instrument like that of E. Wiegel[154] makes evident a really strong influence of pH changes on the results of leaching. These facts induced H. J. Oel[155] to make a more basic study of the leaching process in model glasses of simplest alkali–Ca silicate composition for a reexamination of the relationship of the leaching intensity as a function of pH, but without taking into account the behavior of silicic acid, in principal agreement with numerous data known from the literature on leaching mechanisms.

510. Later, H. J. Oel[156] investigated the leaching reactions of enamels and glazes in connection with the equilibrium conditions existing between the acid and alkaline ranges of the solvent and the pH indicated in contact with powdered samples. In the acid range, there was a relatively wide variability in the degree of leaching as in correlation with the composition of glazes or frits. In the alkaline range, however, the degree of leaching, in general, proved to be similar to that of the acid range, but

[152] *Mitt. Ver. Deut. Emailfachleute* **12**, (5), 27–32 (1964).
[153] *Glastech. Ber.* **29**, (4), 131–151 (1956).
[154] *Glastech. Ber.* **29**, (4), 137–144 (1956).
[155] Congr. *Int.* 7th, Bruxelles, juin/juillet, 1965, Sect. **16**, 1–5.
[156] *Ber. Deut. Keram. Ges.* **45**, (6), 305–309 (1968).

the glazes were relatively *more* leached than the frits, and the differences among individual glazes were lower than they are in the acid range (cf. Vol. V.B. ¶ 82).

511. From the aspect of glass production technology, it is interesting to learn that the natural glassy rock species "perlite" (cf. Vol. IV.A. ¶ ff.) is an attractive raw material for the manufacture of special glasses. K. S. Kutatelyatdze and R. D. Verulashvili[157] examined the direct use of the abundant Armenian perlite as the basis for production of high-voltage glass insulator bodies. The application of perlite profits from the relatively markedly lower temperatures of fusion in the glass furnace operation which is a considerable economic advantage, and the excellent electric properties of perlite even when the alkali content of the batches is at an optimum ratio of $Na_2O:K_2O$. The observations here published are confirmed by M. G. Manvelyan, S. F. Rustambekyan, and A. F. Melik-Akhnataryan,[158] who also started with Armenian perlite as the raw material, but molten in this case in an electric heated glass tank furnace. A strong evolution of foam may become highly troublesome in the fusion operation when only perlite is in the batch composition, but this defect can easily be overcome by the addition of 10 to 15 wt % quartz to the batch. All information on the technological usability of perlite in Russian glass plants confirms this favorable experience, especially with suction gathering machines for container glass (relatively high in alumina).

512. H. J. Oel[159] reexamined the leaching of glazes and enamels to ascertain the equilibrium conditions existing between the acid and alkaline ranges of the solvent, as indicated by the pH on contacts with powdered samples. In the acid range, there was a rather wide variability in the degree of etching, in correlation with the composition of the glaze or frits. In the alkaline range, in general, the degree of leaching proved to be similar to that of the acid range; however, the glazes were relatively *more* leached than the frits, and differences among the various glazes were not as wide as that in the acid range (cf. Vol. II.B. ¶ 196).

[157] *Steklo Keram.* **23**, (5/6), 241–244 (1966); see also a recent review by K. S. Kutateladze, R. F. Verulashvili, and S. N. Papuashvili, *Verres Refract.* **26**, (6), 153–160 (1972), with many instructive details and diagrams on siliceous volcanic rocks as raw material for glass manufacture.

[158] *Verres Refract.* **25**, (5/6), 294–295 (1964).

[159] *Ber. Deut. Keram. Ges.* **45**, (6), 306–309 (1966).

Chapter VI

Spontaneous and Controlled Crystallization in Glass

DEVITRIFICATION OF GLASS "STONES" AND THEIR CONSTITUENTS

513. The rich literature existing on the phenomena of glass crystallization, commonly called its devitrification, as a physical-chemical sequence of different steps is the subject of the Vol. III.A of our series. Thus, we may restrict our present text to report only the technological phenomena of undesirable changes in appearance of glass by devitrification, and not discuss the elementary process of structural nucleation and crystal growth. We will describe their general morphological characteristics and material testing properties, and give a brief classification of the different sources of crystalline inclusions in glass, including the formation of so-called "stones" as the residual products of reactions between the molten glass bath and the refractory walls in the furnace, and of other details in the fusion, fining, and shaping procedures of the greatest technological importance.

514. Before we enter the preferably descriptive subjects of devitrification phenomena, we may speak of the classical methods for *identification* of the crystallization and reaction products when the flowing glass is nucleated by crystallization centers and agglomerations, chiefly by the classical mineralogical-petrographic determination methods of silicate rocks. We restrict our reports to only a few special articles designated for the use of glass engineers, beginning with the excellent handbook review published by H. Jebsen-Marwedel,[1] with a wealth of instructive micrographs, as a general introduction. A short, general survey of the uses of the mineralogical *polarization microscope* in the laboratory and for a control of glass production was later presented by R. Barta and A. Grenar,[2] with micrographs as very good paradigmata from glass testing results.

[1] In the Microscopy of Silicates, "Handbuch der Mikroskopie in der Technik," (H. Freund, ed.), Vol. IV, pp. 3–87, Umschau Frankfurt/Main, 1967.

[2] *Jena Rev.* **10**, (6), 307–317 (1965).

515. J. Moreau[3] emphasized the special advantages of microscopy in reflected light for all kinds of examination and identification of crystalline inclusions in glass, especially when residual refractory material though more or less changed in mineralogical composition is suspended in glass melts or in entire corrosion zones on contacts between the melts with the tank furnace linings. In the evolution of advanced modern physical testing methods and material technology, the current combination of the optical microscope with the possibilities opened by the *electron-beam microprobe* is of particular significance. This offers advanced micromethods and profile developments in microscopic techniques for the distinction not only of the mechanisms of stone evolution but also of phase transitions like that of β-alumina in electrofused Corhart blocks, inverted into α-alumina (corundum) in grains of a typically secondary origin, as indicated by the smallest alveoli and described by P. Robijn;[4] or the crystallization of $6CaO \cdot Al_2O_3$ in melts derived from the roofs of glass furnace arches; or different morphological evolutions of baddeleyite (ZrO_2) from the superstructure, and the walls in lower portions of the tank furnace; the latter in spicular forms suspended in a highly viscous reaction glass.

516. A special listing of crystalline inclusions and their mineralogical and chemical composition was worked out by R. Katzschmann,[5] including striae (cords) of most variable appearance (shown in micrographs); also devitrification products like feldspar in crystallites from corrosion of fireclay material, cristobalite from borosilicate glasses, in variable shapes, and tridymite, cordierite, $BaO \cdot 2SiO_2$, $BaO \cdot Al_2O_3 \cdot 2SiO_2$ (celsian), $BaO \cdot TiO_2 \cdot SiO_2$, as the most characteristic species of this provenience. The chief aim of the descriptions is at a systematic identification of newly formed silicate minerals, and to indicate different sources of anomalies in the fusion of the batch and fining process of the glass.[6] Katzschmann[7] also studied by optical microscopy and measurements the most important parameters of different Ba-borosilicate glasses in which La_2O_3 and ThO_2 in the ratio 1:1 substitute for a portion of BaO. Such glasses show the lowest speed of crystallization and liquidus temperatures; low amounts of alumina act in the same direction.

517. For the mineralogical and chemical composition of stones in glass, one may examine the extensive data collected with 78 micrographs (some in color) and published by T. Ono and T. Fukui.[8] It is a most recent comparative collection of

[3] *Verres Refract.* **24**, (6), 235–241 (1970).

[4] *Ber. Deut. Keram. Ges.* **42**, (5), 193–196 (1965).

[5] *Silikattechnik*, **17**, (5), 145–149 (1966); **17**, (6), 186–188 (1966).

[6] Cf. III.B. ¶ 96 f., 298; R. G. Grebenshchikov and N. A. Toropov, *Izv. Akad. Nauk SSSR, Otd. Khim. Neorgan. Mater.*, (4), 545–553 (1962).

[7] *Glass Technol.* **6**, (5), 156–160 (1965).

[8] *Asahi Garasu Kenkyu Hokoku*, **22**, (1), 61–98 (1972).

identification material, tabulated data, and of the sources from which they were derived in the glass plant, with particular reference also to cold-repair period formations, and the post-service examination of the refractory bricks used in glass furnaces.

518. For simple Na–Ca silicate glasses, one may use the crystallization data collected by V. I. Shelyubskiĭ[9] which indicate a minimum of crystallization tendencies for the concentration ranges from 19 to 21 mole % Na_2O and 7 to 8 mole % CaO, and interesting R_2O, $4SiO_2$ glasses (with R = Li, Na, K), with CaO contents of 4.5 mole % constant.

519. The application of the electron-beam microprobe for the identification of glass crystallization products was demonstrated by R. V. Adams, M. Rawson, D. G. Fisher, and P. Worthington,[10] with a quantitative determination of UO_2, ZrO_2, and Al_2O_3 in cords of an alkali borosilicate glass, in comparison with wet-chemical analytical data. In the same direction, J. P. Hazart[11] and E. Weinryb gave valuable recommendations for the analysis of glass defects (solid inclusions preferably). On the other hand, M. Schneegans[12] reported on very satisfactory results from *spectrographic* identification and determinations of composition of inclusions by ultraviolet adsorption analysis and X-ray fluorescence, with examples of practical observations in the technological operations.

520. Rich practical experience from glass production processes is offered by M. Bartuška.[13] The use of reflected light in microscopy, and particularly of the modern phase contrast methods, is extensively described and vigorously recommended. Practical examples are also presented[14] by Bartuška to show possibilities for drawing conclusions from textural details as to the presence of different phases of inversions (as demonstrated for ZrO_2 in a primary, secondary, and a colloid-dispersed shape) which are highly valuable for reconstruction of the origin and local conditions of stone evolution, with rapid and accurate laboratory operations.

521. M. Bartuška[15] also shows the conversion from very dense zircon, $ZrSiO_4$, plates in the bottom portion of a high-duty glass tank furnace, with a strong crystallization of baddeleyite in the shape of the well-known "rice-grains." Only a very densely compacted, nearly pore-free refractory material of this group (cf. V.B.

[9] *Dokl. Akad. Nauk.* SSSR **171**, (2), 333–336 (1966).

[10] *Glass Technol.* **7**, (3), 98–105 (1966).

[11] *Verres Refract.* **22**, (2), 145–162 (1968); J. P. Hazart, *Silicates Ind.* **34**, (10), 269–275 (1968).

[12] *Silicates Ind.* **32**, (1), 5–21 (1967).

[13] *Sb., Vys. Sk. Chemickotechnol. Praze, Anorgan. Chem. Technol.* **B.10**, 5–35 (1967); **B.13**, 169–201 (1969).

[14] *Sklar Keram.* **18**, (6), 152–155 (1968).

[15] *Sklar Keram.* **19**, (1), 5–6 (1969).

¶ 166) successfully resists such a service when the glass is relatively high in Alkali. M. Bartuška, J. Ružek, and Gr. Zilná[16] described the crystallization of ZrO_2 and corundum from fusion-cast refractories of this type, with a maximum crystallization speed at 1300° to 1400°C.[17]

522. The same problems of corrosion phenomena with melt-cast zirconia–alumina refractories by Na–Ca silicate glass melts are discussed by H. Woelk,[18] with technological details (cf. Vol. V.B. ¶ 96 f.).

Interesting methods for the determination of devitrification curves from *X-ray diffraction analysis* at elevated temperatures were made by G. Cevales,[19] based on quenched glass samples exposed at varied .temperatures and exposure times. Normally, the devitrification starts from the surface of the samples (cf. Vol. III.A. ¶ 29 ff.); these may be compacted powders, but they can also be fibers in which, for example, devitrite, $Na_2O \cdot 3CaO \cdot 6SiO_2$, and anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$, were identified among the crystallization products.

523. Chromite, as derived from basic refractories of the chrome-magnesite type (cf. Vol. V.B. ¶ 109, 132) and usually observed in special burner refractory bricks of glass tank furnaces, in individual crystallites, is described by H. Jammernegg[20]; chromite is a well known to be a source of stubborn troubles in glass melting operation, because of its very high thermal and corrosion durability.

524. A very peculiar, special open question has arisen over the alleged *absence* of devitrification on gas bubble surfaces suspended in glass melts, as described by J. E. Neely and F. M. Ernsberger.[21] There has been much debating of this possibility defended, with serious differences between statements from W. A. Weyl and G. W. Morey. Experiments in the heating microscope and observations made by Neely and Ernsberger could not disclose definite and unquestionable results, and found no anomalies on the phase boundaries between gas bubbles and glass melt. It is not improbable that, if ever observed, local devitrification might be caused by local volatilization from the melt surface, whereas, internal devitrification is evident as an independent phenomenon. A really *positive* answer to the pending problem of crystal growth on bubble surfaces in glass, however, was most probably disclosed by C. G. Bergeron and J. P. DeLuca[22] for a lead borosilicate glass in which crystals of $PbTiO_3$ had formed on the glass surface, and on surfaces of numerous interior

[16] *Silikaty*, **14**, (5), 131–139 (1970).
[17] See also M. Bartuška and V. Havránek, *Silikattechnik* **21**, (9), 306–313 (1970).
[18] *Ber. Deut. Keram. Ges.* **43**, (1), 109–11 (1966).
[19] *Vetro Silicati* **10**, (4), (58), 5–111 (1966).
[20] *Glastech. Ber.* **39**, (9), 403–409 (1966).
[21] *J. Amer. Ceram. Soc.* **49**, (7), 396–397 (1966); see also III.A. ¶ 30 ff. 44.
[22] *J. Amer. Ceram. Soc.* **50**, (2), 116 ff. (1967).

bubbles and continued to grow after quenching and during cooling. Crystals, however, were never found within the glass except at bubble surfaces.

525. Uncertainties to the role of simultaneous gas bubble evolution and crystallization in glass melts are also found in a previous technological literature, as may be seen from a publication by M. Boffé, G. Pécriau, and E. Plumat[23] describing microscopic devitrification phenomena in Na–Ca silicate glasses (cf. ¶ 296). Bubbles are formed near aggregations of crystals of wollastonite and cristobalite when the atmosphere is water vapor. Explanation of these facts was sought in certain regularities but without any clear success; it is, nevertheless, interesting to know that the interferometric test for the composition of glass cords after J. Löffler indicated slight (2%) shifts in silica content around wollastonite crystallizations in layers of 0.1 μ thickness. On the other hand, the interferometric method of Nomarsky was not able to confirm changes in the refractive index of such cords. Apparently a remelting of the glass favors a secondary evolution of seeds so much the more that crystallites are present which may have initiated release of gas supersaturation in the glass. Noteworthy also is a frequent occurrence of bubbles arranged along circles concentric to wollastonite nodules.

526. Whether high pressures (up to 30 kbar for 20 minutes,) may influence the crystallization temperature of a given glass (e.g., on simple Li silicate glasses of the ratio $Li_2O:SiO_2$ = 1:1.5, to 4.0) was examined by M. Tashiro, S. Sakka, and T. Yamamoto,[24] at temperatures from 600° to 500°C. The qualitative result of X-ray diffraction measurements was to confirm an intense depression of the crystallization temperature when high pressures are applied (cf. Vol. II.A. ¶ 205, 228).

527. When the crystallization rate in glasses is above 50 μ/minute, it is promising to follow the process by the *differential-thermal* analysis (DTA) method, as G. Dusollier and M. Derobert[25] demonstrated. In experiments made with an optical borosilicate glass, it became evident that there are distinct peaks on the diffraction curves which show influences of the rate of heating up, but also of the grain sizes of the glass powder; the finer this powder, the greater a decrease in temperature indicating the exothermic crystallization effect (cf. Vol. III.A. ¶ 105–119). Devitrite and α- and β-$CaSiO_3$ were the crystal phases, the peaks of which were studied on the diagrams of the DTA. Such studies are of great importance for a control of the production of glass-ceramics, and for metal/glass sealings in which the glass is commonly fine powdered and rapid sintering.[26]

[23] Cf. Symp. on Nucleation and Crystallization in Glasses and Melts, pp. 47–54, Amer. Ceram. Soc., 1962.

[24] *Bull. Inst. Chem. Res. Kyoto Univ.* **44**, 401–409 (1966).

[25] *Verres Refract.* **23**, (1), 10–18 (1969).

[26] Cf. W. Sack, H. Scheidler, and J. Petzold, *Glastech. Ber.* **41**, (4), 138–144 (1968).

528. P. S. Rogers and J. Williamson[27] studied the effects of additions of iron oxides to common $CaO-MgO-Al_2O_3$ silicate glasses in which, e.g., Fe_2O_3 distinctly acts as a nucleator for crystallization, following the Turnbull–Fisher equation for the rate in the growth of spinels, Mg (Al, $Fe^{III})_2O_4$, as the primary phase (besides diopside which is metastable and is changed to form in the glass melilite and gehlenite). The nucleation curves in G. Tamann's classical interpretation showed a maximum of 750°C for Fe_2O_3 contents of the glass varying between 7 to 13 wt %, the activation energy of nucleation being 100 to 120 kcal/mole (cf. Vol. II.C. ¶ 7 ff.).

529. In zinc-aluminosilicate glasses, P. W. McMillan, G. Partridge, and J. G. Darrant[28] observed in the heating microscope over the range from 700° to 1500°C the crystallization of willemite (Zn_2SiO_4), zinc spinel $ZnAl_2O_4$, cristobalite, and a tetragonal, "stuffed" *keatite* phase (written as $ZnO \cdot ZnO \cdot SiO_2$). The formation of this latter compound is dependent on small additions of alkalies and alkaline earths, and quite specific oxides of tri-, tetra-, and pentavalent metals. It is remarkable that quite different rates of crystallization indicate apparent changes in the structural nature of the phases mentioned here, although the activation energy of crystal growth remained nearly constant (cf. Vol. III.B. ¶ 339). The stuffed keatite phase breaks down to form willemite at about 1000°C.

530. The superstructure of glass tank furnaces has been called repeatedly a constant source for originating typical glass defects (cf. ¶ 499) and, therefore, here again we may cite the observations published by J. Daudans, A. Krings, and A. Sevin,[29] with many micrographs and technological details (cf. Vol. V.B. ¶ 113).

531. M. Tornati, C. Moretti, and G. Bonetti[30] described corrosion of fusion-cast $Al_2O_3-ZrO_2-SiO_2$ refractory blocks from the walls of feeder channel systems in a furnace for borosilicate glass (for pharmaceutical purposes) after a period of service over 24 months. In the thorough microscopic analysis of the reaction zones, it was particularly interesting that a highly silicic, alkali-poor layer had been formed, evidently by glass migration towards the refractory walls. In this zone, corundum is redissolved and the tendency for the development of silica cords is therefore, imminent. Such extremely limpid silicic cords are ideal test subjects for A. Winter's highly sensitive light diffraction method of testing glass, and the detection of the slightest heterogeneities, as she described these,[31] in combination with a double-

[27] *Glass Technol.* **10**, (5), 128–133 (1969).
[28] *Phys. Chem. Glasses* **10**, (4), 153–158 (1969).
[29] *Glastech. Ber.* **42**, (10), 391–395 (1969).
[30] *Vetro Silicati* **12**, (2), (68), 5–10 (1968).
[31] *Verres Refract.* **21**, (3), 191–195 (1967); **21**, (6), 509–518 (1967).

beam photometer, and secondary electro multipliers for measurements of the 90° Rayleigh scattering intensity. Data of such measurements are particularly useful for the detection of domains in the glass which have the potential to evolve bubbles in late stages of fining and cooling thereafter (cf. ¶ 89). For this reason, the observations and data of A. Winter are of high significance for optical glass production.[32]

532. X-ray fluorescence (microluminescence) examination was recommended by J. P. Fieck and J. B. Debuisser[33] as especially useful when inclusion crystallites of ZrO_2 or $ZrSiO_4$ from refractory blocks or nonassimilated inclusions from chromite particles in glass are to be identified by a "microprobe" analyzer according to C. Legrand, H. Gondet, and A. Rose,[34] and in combination with a scanning microscope,[35] as demonstrated for identification and analysis of ZrO_2 crystallites, chromite, but also black granulates formed by the reduction of CdSe-colored glass. The microfluorescence method is superior to normal X-ray fluorescence, as demonstrated for such erratic material in glass as fragments of tools made of Fe—Ni—Cr alloys (stainless steel), and as a "macro" probe in the kind of Castaing's principles, of surprising simplicity for rapidity in routine work. The useful field for the application of the macroprobe techniques is about 1 mm^2.

533. H. E. Schwiete and N. B. Das Gupta[36] gave a comprehensive report on all kinds of contact reactions between glass melts and refractories, especially of the fusion-cast ZAC type (cf. Vol. V.B. ¶ 96 f.) with a typical glass matrix of its own. The experimental studies were extended to the mechanism of the resorption (assimilation) on the contacts, and the evolution of bubbles ("seeds" in the glass) when temperatures above 1000°C are reached. ZAC blocks evolve more seeds than do mullite blocks with their higher contents of glass matrix and of SO_3.[37]

534. For a similar report on the use of baddeleyite-corundum refractories of the type discussed above, we cite here also J. Ružek[38] who described, from ceramic technological viewpoints, thermal expansion and other volume changes of such material in service, as well as their volume stability and the reaction behavior of the

[32] Cf. L. Prod'homme, *Rev. Opt. Theor. Instrum.* **45**, (4), 163 ff. (1966); It is an often observed fact that such melts, e.g. of Ba Crown glass, are practically never entirely free from heterogeneities when molten in platinum containers.

[33] *Verres Refract.* **22**, (4), 375–384 (1968).

[34] Congr. Int. Opt. Rayons X, et la Microanalyse, 4th Orsay, 1965.

[35] Cf. M. Schneegans, *Silicates Ind.* **32**, (1), 15–21 (1967).

[36] Forschg. Ber. d. Landes Niederrhein u. Westphalen, No. 1885, 117 pp., Westdeutsch. Verlag, Köln-Obladen, 1968; s.a. *Sprechsaal* **102**, (20), 869–872, 874 (1969).

[37] See also Vortrags-Veröffentl. Haus d.Technik, Essen, Report No. 77, pp. 139–154, 1968, on the use of fusion-cast refractories in glass and steel industries.

[38] *Silikaty*, **12**, (1), 31–41 (1968); **12**, (2), 123–136 (1968).

matrix glass phase in a reducing fire (cf. Vol. V.B. ¶ 169). The thermal changes are caused chiefly by the volume effects of the inversion of tetragonal into monoclinic ZrO_2 modification. Metal oxidation which often occurs in the strongly reducing atmosphere of the fusion-casting process may be the origin of late reactions when the refractory materials come into contact with the glass bath in the tank furnace, staining the glass first gray, and later yellow by oxidation. Such changes may be combined, moreover, with crystallization at temperatures above 1200°C and over longer periods in the contact zones.

M. Bartuška[39] described details on stones or the contact zones mentioned above, by microscopic measurements and micrographs, with repeated descriptions of ZrO_2 and $ZrSiO_4$ in different shapes, and crystallization particularities (¶ 520 f).

535. We do not want to omit a recommendation to our readers to make themselves familiar with an excellent recent report by N. N. Sheftal'[40] of which we have to speak further in Vol. III.A. ¶ 58–65 of our Series.[41]

536. In the direction to *slag* equilibria and crystallization (cf. Vol. II.C. ¶ 8) we emphasize investigations made by J. Williamson, A. J. Tipple, and P. S. Rogers[42] on the influence of iron oxides on the kinetics of crystal growth in glasses of the quaternary system $CaO-MgO-Al_2O_3-SiO_2$. The crystal growth rates in such glasses are proportional to the squares of the concentration in FeO; with increasing temperatures of crystallization and increasing ratios Fe^{II}/Fe^{III}, the rate of crystallization deviates from linearity at constant temperature.

REPRESENTATIVE LITERATURE REFERENCES ON CRYSTALLIZATION IN GLASSES OF DIVERSIFIED CHARACTERISTICS

537. From Vol. VI.C. ¶ 53 ff.), we learned that Au-, Ag-, or Cu-containing dispersoid glasses may show *photosensitivity*, and may be used for new ways of photoimaging in glass. Experiments made by E. V. Gurkovskiĭ[43] confirm the close kinship

[39] *Sklar Keram.* **18**, (6), 152–155 (1968).

[40] After five contributions made to a Sympos. on the "Growth of Crystals" in the 3rd Conf. on Crystal Growth and the Synthetic Crystal Growth of Silicates of Direct Importance (J. E. S. Bradley, Engl. transl., Consultants Bureau, 1968), Parts V.A.a.B.

[41] A well-oriented abstract was written by H. Wondratschek, *Glastech. Ber.* **42**, (11), 487 (1969); **43**, (4), 162 (1970), with particular reference to glass problems of nucleation and crystallization in the latter report, in all parts with valuable references to more difficultly available literature.

[42] *J. Iron Steel Inst.* **206**, 898–903 (1968).

[43] Vitreous State and Catalyzed Crystallization of Glass, Moscow, Akad. Nauk SSSR, 1963 (Engl. transl. Consults. Bureau, New York, 1964), pp. 163–165.

of this phenomenon with nucleation and crystallization to develop special glass-ceramics (called "Photocerams"), on which the reader may be informed by an excellent report by W. Vogel.[44] They were discussed by A. I. Berezhnoĭ[45] with particular reference to modern methods of photographic reproduction onto glass for purposes of metal coating, miniaturization of electric switch programs, and the like. Decidedly, it is interesting that V. I. Shel'yubkiĭ[46] observed in ultraviolet-irradiated, CeO_2-sensitized lithium aluminosilicate glass a higher crystallization intensity, and a greater number of silver particles than are identified in the original state of the same glass.[47]

538. Iv. Fanderlik[48] presented a much detailed monographic review on the physical phenomena of photosensitive glasses, in general (see Vol. VII. ¶ 858 ff.), and those of containing silver halogenides nuclei and ultramicronic crystallites, in particular (cf. Vol. VI.C. ¶ 151, 155 ff.), for changes in the evolution and destruction of color centers and the spectroscopic characteristics as a function of irradiation effects. Of particular interest are photosensitive glasses containing rare-earth elements, chiefly Ce and Eu which show photochromic activity without nucleation; also glasses with organic interlayers, e.g., trimethyl 1, 2, 3 indoline-spiro 2′nitro-6′benzo (b) pyrane, used for the manufacturing of sun radiation protection goggles, or the construction of electronic storage cells with automatic rejection of information, for photometers, and integration diaphragmata, for holography, and laser techniques. The kinetics of evolution and destruction reactions of color centers in photochromic Ag-halogenide-containing glasses are discussed, in addition, by Fanderlik.[49] The equilibrium of evolution and destruction of color centers is dynamic, the activated state of increased energy, the transition into that of lower energy being a typical relaxation mechanism.

539. Unusually *refractory*, partially crystalline Vanadiumoxide (VO_4)–silica

[44] "Structure and Crystallization of Glasses," Chapter 8, 1, 2, pp. 163 ff. Deut. Verlag Grundstoff-Ind., Leipzig, 1965, may be recommended; furthermore: P. Schleifer, Mar. Boczuch–Laczka, and W. Bazan, *Szkło Ceram.* **19**, (12), 361–362 (1968). We come back to these photosensitive glasses, and their methods of production, in Vol. III.A. ¶ 39 ff., 44 ff.

[45] In his book "Glass Ceramics and Photo-Sitalls," Mashinostroenie, Moscow, 1966 (Engl. transl. Plenum, New York, 1970), Chapter III, pp. 125–192.

[46] *Dokl. Akad. Nauk SSSR* **171**, (3), 580–582 (1966).

[47] See also A. I. Berezhnoĭ and Yu. M. Polukhin, *Izv. Akad. Nauk SSSR, Neorgan. Khim.* **3**, (6), 986–992 (1967).

[48] *Informativni Prehled Veda a Vyskum prum Sklarskem*, ČSR **12**, (4), 65 pp. (1969); abstr. *Glastech. Ber.* **45**, (3), 110 f. (1972).

[49] *Silikaty* **14**, 197–210, (1970); cf. theoretical calculations by P. G. Smith, Congrès Internatl. du Verre, 7th, Bruxelles C. R. *Acad. Sci.* **III**, 2/108, 1–9 (1965).

glasses are described by S. D. Brown and S. S. Kistler,[50] of such a high degree of refractoriness that they could not be drawn into fibers by the heat of flames which are so commonly used for silica. Such glasses are blue, or even black, with a VO_4 content of 0.5 to 1.5/100 SiO_2/brown with 5/100 in ratio. The crystallinity is caused by cristobalite; the viscosity of the matrix glass is very high; the surface of the drawn samples looks typically "glazed"; above 2000°C the viscosity is comparable to that of normal silica glass. High thermal emissivity is characteristic of such VO_4-containing silica glasses.

540. A series of excellent contributions to this field is found in a recent "Symposium of the Vitreous State of Catalyzed Crystallization of Glass,"[51] namely:

A. A. Gorbachev, Yu. M. Polukhin, A. M. Ravich, and L. M. Yusim[52] on optical measurements in photosensitive glass (cf. Vol. VI.C. ¶ 90);

N. A. Shmeleva, V. G. Chistoserdov, and A. I. Gerazimova,[53] on the action of dilute HF solution on Li silicate glasses;

V. A. Sharaĭ, N. N. Ermolenko, and I. G. Lukinskaya,[54] on crystallization of glasses in the system $Na_2O-Fe_2O_3-SiO_2$, with particular reference to problems of glass-ceramics (cf. Vol. III.B. ¶ 371, footnote 557);[55]

V. S. Nikandrov,[56] on the crystallization of "catalyzed" (mineralized) alkali-free glasses;

A. A. Zhunina, V. N. Sharaĭ, V. F. Tsitko, and A. N. Khripkova[57] on crystallization of glasses of the system $CaO-MgO-Al_2O_3-SiO_2$, in the presence of Cr_2O_3, with the formation of an interesting stable pyroxene phase (cf. Vol. III.B. ¶ 300).

N. P. Danilova,[58] on the crystallization of $Na_2O-CaO-MgO-Al_2O_3-SiO_2$ glasses, in definite regions of the phase diagram (cf. III.A. 39 footnote 49).

I. S. Kachan and Z. I. Shalimo,[59] corresponding studies on the system $CaO-BaO-Al_2O_3-SiO_2$, and the physical properties of the crystalline phases.

[50] "Symposium on Nucleation and Crystallization in Glasses and Melts," pp. 35–36, Amer. Ceram. Soc. Columbus, Ohio, 1962.

[51] Akad. Nauk SSSR, Moscow, 1963 (Engl. transl.: Plenum, New York, 1964).

[52] Reference 51, pp. 166–168.

[53] Reference 51, pp. 169–171.

[54] Reference 51, pp. 180–182.

[55] Cf. J. Williamson and P. S. Rogers, Conf. Silicate Industry (Siliconf.), 7th, Budapest, 1967, pp. 525–532, Akademiai Kiado, Budapest, 1968.

[56] Reference 51, pp. 188–191.

[57] Reference 51, pp. 192–194.

[58] Reference 51, pp. 195–197.

[59] Reference 51, pp. 198–199.

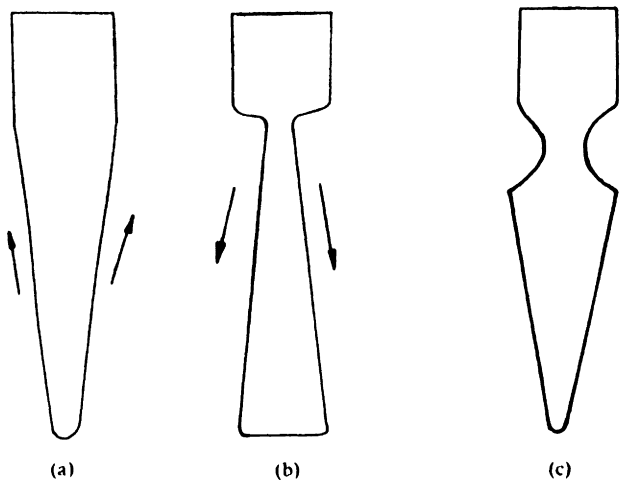


FIG. 120. Dissolution shapes (a) when the rod sample is lighter than the glass and flows upward; (b) when the sample (e.g., a corundum monocrystal rod) is heavier, fresh glass melt attacks at the top; (c) profile obtained in melt of lead silicate glass; such a shape cannot be explained only by density conditions. (Busby and Eccles.)

G. A. Pavlova and V. G. Chistoserdov,[60] on the electric properties of alkali-free glasses as a function of composition and thermal history.

541. Other studies made by T. S. Busby and J. Eccles[61] apply to the dissolution of single crystals of *corundum* in molten glasses of technological interest, e.g., the special "*E*" glass for fiber production, and others of Cabal type. It is particularly noteworthy how different the redissolution may be locally developed either on the "metal line," or more uniformly over the entire length, and the different flow direction of the reaction glass, down or upwards for a borosilicate glass, or a Pb silicate glass, respectively (cf. Fig. 120).

The rare occurrence of well-developed *quartz* crystals in furnace devitrification products in an $Na_2O-CaO-MgO$ silicate (bulb) glass is described by T. Kishii,[62] in paragenesis with tridymite, devitrite, and other phases of the system $Na_2O-CaO-SiO_2$, the quartz being mostly associated with diopside and albite.

542. Y. Suzuki and K. Muranaka[63] discussed the devitrification of glasses of the

[60] Reference 51, pp. 200–204.
[61] *Glass Technol.* **5**, (3), 115–123 (1964).
[62] *J. Ceram. Ass. Jap.* **71**, 177–181 (1963).
[63] *Asahi Garasu Kenkyu Hokoku* **14**, (1), 1–15 (1969).

system $Na_2O - CaO - MgO - Al_2O_3 - SiO_2$ with about the same mineral associations (quartz usually being absent), using the G. H. Grauer and E. H. Hamilton temperature gradient method (1950 as a modification of the I. F. Ponomarev device) (¶ 413). The same authors[64] studied the effects of minor constituents of sheet glass on its devitrification behavior, with relatively high effects for Li_2O, P_2O_5, TiO_2, As_2O_5, and B_2O_3. The number of wollastonite nuclei increases with the rate of crystal growth when Li_2O is added.

543. *Spherulites* in silicate glasses as crystal growth phenomena were studied in the electron microscope by M. G. Degen and N. A. Toropov[65] who found in the central portions particles of 0.05 to 0.07 μ in diameter which grow to individual crystals of 1 to 2 μ in diameter, following typical laws of polymerization for organic compounds and natural minerals (cf. Vol. III.A. ¶ 30 ff.), and the same principles of geometric selection.

Using the gradient method for phases of the system $BaO - TiO_2 - SiO_2$ in an optical flint glass, Uta Hoff and R. Katzschmann[66] made fascinating observations by direct measurements of the crystal growth rates on the surface of the glass, and on contacts of glass with platinum (cf. Vol. III.A. 68 ff.).

544. *Labradorite* and *cordierite* are interesting devitrification products in glasses of the commonly applied system $Na_2O - CaO - MgO - Al_2O_3 - SiO_2$, as studied by St. Lyng,[67] using NaF as the mineralizing agent, and electron microscopy for studies of complex separation of microphases (cf. Vol. III.B. 289 ff.), in a surprisingly fine-crystalline state.

Concerning newly formed minerals like baddeleyite, nepheline, and feldspars in crystalline inclusions in glass, we again cite the observations made by A. Sevin and J. Daudans[68] (cf. ¶ 496, 499, 530).

V. A. Dorofeev, V. A. Movlav, and M. A. Našelski[69] transferred control methods for electric conductivity measurements used in glass practice, to that for *basalt* melts which have a high technological significance for melt-castings of paving bricks or gutter grooves for steel casting, runners, and the like (cf. Vol. II.C. ¶ 8 ff.).

545. Preferably, feldspars and glass matrix are the constituents of glass-ceramics of the system $Na_2O - BaO - Al_2O_3 - SiO_2$, as developed by D. A. Duke, J. E. Megles, J. F. MacDowell, and H. F. Bopp,[70] and which contains another glass matrix with

[64] *Asahi Garasu Kenkyu Hokoku* **14**, (2), 59–70 (1969).
[65] *Izv. Akad. Nauk SSSR Ser. Neorgan. Mater.* **2**, (9), 1391–1394 (1966).
[66] *Silikattechnik* **17**, (9), 285–290 (1966).
[67] *Glastech. Ber.* **40**, (4), 136–140 (1967).
[68] *Glass Technol.* **8** (4), 103–107 (1967).
[69] *Silikaty*, **17**, (10), 292–293 (1967).
[70] *J. Amer. Ceram. Soc.* **51**, (2), 98–102 (1968).

celsian. This glaze and the glass-ceramic itself as a unit has a remarkably high mechanical strength derived from the application of a compressive inner strengthening (stress-created) effect.

546. With reference to photosensitive Li silicate glasses (cf. ¶ 531, 546), M. Noshiro and Y. Jitsugiri[71] disclose the infrared transmission analysis of crystalline Li_2SiO_3 (indicated by the absorption band at 851 cm^{-1}) and $Li_2Si_2O_5$ (at 643 cm^{-1}) to calculate the percentage of crystallinity as a fundamental factor. The infrared data are in good agreement with those presented by A. N. Lazarev and V. A. Florinskaya.[72]

547. We also mention again the results of V. Gottardi, G. Bonetti, and M. Nicoletti,[73] and their recommendation that it is essential to consider the thermal history of devitrification phenomena in technological testing. F. E. Wagstaff[74] gives evidence that the crystallization of cristobalite in *silica* glass is metastable since the high- (α-) cristobalite structure is still preserved as "undercooled" in the inner portions of the glass samples, whereas the exterior portions already show the stable low-temperature (β-) modification; the inversion $\alpha \rightleftharpoons \beta$ is spontaneously released as soon as inner stresses are eliminated.

548. F. E. Wagstaff[75] detailed a complete analysis of the kinetics of crystallization and fusion of cristobalite by a simple equation $\mu = A\,\Delta T/\eta$ (with η = viscosity, μ = the rate of crystal growth, and A = a constant) for the crystal growth. The process is continuously controlled microscopically in its morphological development (between 1347° and 1618°C). The temperature is then raised to the fusion point, the rate of growth being strictly linear at 1704°C (cf. Vol. III.A. ¶ 29 ff., 47 ff.; Vol. III.B. ¶ 14 ff.).

549. A special investigation on phase boundaries and crystallization phenomena in *silica glass* coming into contact with melts of common glass, was made by J. Matej and Marie Truhlářová.[76] On such contacts, as a rule, two layers were observed, one on immediate contact, characterized by a cristobalite layer in the state of inversion, the other a silica-enriched diffusion product from the underlying Na – Ca silicate glass. The devitrification of the latter is relatively late, i.e., it takes place during the cooling process.

550. *Fissurization* in opalescent borosilicate glasses in an early stage of devitrification was described by G. C. Kuczynski and J. Herbert,[77] combined with a

[71] *Asahi Garasu Kenkyu Hokoku* **18**, (2), 59–70 (1968).
[72] *Struct. Glass* **9**, pp. 9 ff. (1966).
[73] *Verres Refract.* **22**, (6), 589–594 (1968); *Vetro Silicati* **11**, (3), (63), 5–12 (1969) (cf. VII. ¶ 578).
[74] *Phys. Chem. Glasses* **10**, (2), 50–53 (1969).
[75] *J. Amer. Ceram. Soc.* **52**, (12), 650–654 (1969).
[76] *Silikaty* **13**, (4), 291–299 (1969).
[77] *Verres Refract.* **23**, (6), 675–678 (1969).

detailed mathematical treatment of the formation of a very thin surface layer on such a glass, and the background of the micro-cracking phenomena (cf. VII. ¶ 924); again, cristobalite was the primary crystallization phase. The cracking follows the classical Griffith theory. The specific action of small additions of *fluorides* was explained by S. Lyng, J. Markali, J. Krogh-Moe, and N. H. Lundberg[78] for the multi-component system (Li, Na, $K)_2O-(Ca, Mg, Zn)O-Al_2O_3-SiO_2$ in which an intermediate crystallization of a *fluoromica* (cf. Vol. IV.A. ¶ 165 ff.) is observed, followed by volume crystallization of other crystalline phases which show a transition of the glass-ceramics of a very compact texture and therefore high mechanical strength.

551. The very close kinship of such reactions of crystallization phenomena in glasses with those of *cation exchange* from a given glass with salt melts will not be discussed here, except a brief reference to recent publications which may be helpful for an approximation of the recent level of our theoretical and practical knowledge of this highly significant problem:

B. Locardi and A. Lama[79] take the general approach to the simple silicate and alkali aluminosilicate glass melts in cation exchange with molten salts, as can be seen in its application to the glass "strengthening" process (cf. Vol. VII. ¶ 899–905).

V. V. Moĭseev, T. V. Permyakova, and M. N. Plotnikova,[80] see more from the viewpoints of exchanges with aqueous solutions in the place of salt melts and their practical application.

P. S. Roberts and J. Williamson[81] examine the crystal growth kinetics in ZnO-containing aluminosilicate glasses (cf. ¶ 528 f.).

OPALESCENCE AND OPACITY OF GLASSES CONTAINING FLUORIDES

552. An important early publication on the nature of opalescence and turbidity evolving particles in *fluoride–phosphate* glasses was presented by S. I. Sil'vestrovich and E. M. Rabinovich.[82] Such opaque glasses contain the fluorine as AlF_3; cryolite, Na_3AlF_6; chiolite, $5NaF \cdot 3AlF_3$; and NaF. In corresponding potassium glasses only KF was observed in the X-ray diffraction patterns. Such phosphate glasses contain ultramicroscopic particles in sizes between 1 to 6 μ in diameter which are the source

[78] *Phys. Chem. Glasses* **11**, (1), 6–10 (1970).
[79] *Phys. Chem. Glasses* **11**, (3), 71–74 (1970).
[80] *Glass Technol.* **11**, (1), 6–9 (1970).
[81] *Verres Refract.* **26**, (2), 53–56 (1972).
[82] *Zh. Prikl. Khim.* **32**, 1690–1695 (1959).

of the opalescence. Phosphate glasses which contain Na and Al but also Ca and Mg in the form of the ortho-, meta-, and pyrophosphate molecules, show smaller particles (order of magnitude down to 0.5 μ) as a function of the acidity of the matrix glass. Phosphate-free silicate Na + Ca and fluoride glasses prepared by additions of Na_2SiF_6 and CaF_2 to the batch compositions develop, as a technological rule, a desirably good degree of opacity but are not easily introduced into practical use when flashed together with other glasses because the usually different coefficients of thermal expansion cause cracking, as it was experimentally studied by V. V. Vargin.[83] The separation of crystallization products (cristobalite, fluoroaluminates, and colored pigment phases like CdS) introduce heterogeneities and therefore increase the cracking tendencies.

553. More recently, H. Rötger[84] developed a comprehensive *kinetic theory* of the turbidity causing phases in fluorosilicate glasses, based on the crystal growth on undercooling, and on optical measurements of light diffraction for the absorption effects with the wavelengths of the scattered light (C. Rayleigh and M. Planck, 1904; G. Mie, 1910). In practice, it was observed that the scattering relatively diminishes with increasing thickness of the samples, indicating deviations from the theory; the thinner the glass samples, the better the agreement with Rayleigh's theory of scattering effects. However, there still are discrepancies with the classical theories of crystal growth as applied to H. R. Swift (1947) and H. Schönborn (1962), indicating a one-dimensional growth. Light losses caused by such phenomena are by no means caused only by scattering, when absorption became prevailing. With increasing scattering, an intense shifting of the absorption range to longer wavelengths is observed; this means that thinner samples show scattering prevailing at low wavelengths—and vice-versa—as demonstrated in Rötger's experiments.

554. From the viewpoints of opal glass technology, C. R. Das[85] found empirically that a minimum content of opacifying fluorine is 4.5% of the glass weight; below this value, opacity decreases with increasing temperature and time of melting, but for furnace operation, the optimum ratio of fuel/air also is important. The *retention* of F above 4.5% can be improved by introduction of ZnO or K_2O into the glass composition, also of alkaline earths (CaO, BaO), and oxidizing agents. On the other hand, contents higher in alkalies are decidedly detrimental to opacity effects. Replacement of SiO_2 by P_2O_5 in simple Na – Ca silicate glasses must be made with caution to avoid damage to their manufacturing properties; the

[83] *Steklo Keram.* 8–11 (1957) [Engl. transl. *Glass Ceram.* **14**, 236–239 (1960)].
[84] *Silikattechnik* **15**, (1), 71–78 (1964).
[85] *Bull. Centr. Glass Ceram. Res. Inst. (Calcutta)* **11**, (3), 68–71 (1964).

combination P_2O_5 + B_2O_3 gives better opacity. Das[86] gave more detailed instruction for avoiding F losses and for the optimum degree of turbidity as a function of the concentration in F, by a crystallization of the compound $KF \cdot CaF_2$; the introduction of ZnO (see above) favorably influences both factors.

555. Starting from a mathematical formulation of light diffraction effects by *spherical* particles as a function of their diameters,[87] and in comparison with H. Rötger's results (see above), G. Hilbig[88] found for a series of commercial turbid glasses a relatively good agreement in essential points. Beyond the theory of calculation for monodisperse dispersoids, Hilbig attempted to extend the theoretical consideration of polydisperse systems, using advanced optical methods and models for the particle distribution functions of defined statistical probability.

556. Practical viewpoints, e.g., for the manufacturing of pink-colored opal glasses with highly dispersed gold particles, are in the foreground of studies made by G. Paoletti[89] (cf. Vol. VI.C. ¶ 109, 199) who emphasized the indispensable presence of oxidizing agents (KNO_3, As_2O_5) in the melts, for an optimum "ruby effect" at 670°C as the working temperature.

557. The strong *mineralizing* (crystallization catalyzing) *efficiency* of fluorides added to normal glasses of the technologically often preferred system $Na_2O-CaO-MgO-Al_2O_3-SiO_2$, especially in the partial system of andesine-labradorite–Mg silicates, was made evident by St. Lyng;[90] for the manufacture of glass-ceramics in the ranges here concerned, it is particularly important that for a net percentage of fluorine to be applied, the given complex evolves full volume crystallization in different steps: first, a phase unmixing reaction; second, the formation of a complex fluoride in the separation range or on the phase boundaries of different neighboring partial systems; and third, volume crystallization phase which, in the present case, is mostly plagioclase radiating from the primary crystallites (cf. Vol. III.A. ¶ 39; Vol. III.B. ¶ 289 ff.). When less then 5% MgO is present in the glass melt, the crystallization of CaF_2 is primary; when the MgO content is higher, more complex compounds may appear. Sometimes, one may observe very characteristic ipitactic overgrowth of plagioclase over CaF_2 (in well-developed octahedra as was shown in excellent micrographs). We may cite here important discussions of W. Haller and B. Macedo,[91] on phase connectivity in microheterogeneous glass (cf. Vol. VII. ¶ 357).

[86] *Bull. Centr. Glass Ceram. Res. Inst. (Calcutta)* **13**, (4), 101–107 (1966).
[87] Cf. D. C. van de Hulst, "Light Scattering by Small Particles," Wiley, New York, 1957.
[88] *Silikattechnik* **16**, (9), 289–292 (1965).
[89] *Vetro Silicati* **11**, (2), (62), 12–15 (1967).
[90] *Glass Technol.* **9**, (6), 179–184 (1968).
[91] *Phys. Chem. Glasses* **9**, (5), 153–155 (1968).

558. Returning briefly to the *mineralizing effects* of fluorides in glass melts, we refer to K. Vobroník,[92] on dull-color opal glasses, with only about 2.5% F contents, but initiated by the seeding effect of 0.001% Pt for the crystallization of primary NaF (on H. R. Swift's method of crystallization nucleation cf. Vol. II.B. ¶ 203) and a photometric measurement of light transmission losses by scattering. Only in a relatively narrow concentration range for NaF addition, a fully developed turbidity effect is reproducible: this is a fact of tremendous importance for the purposes of illumination technology for testing electric bulb lamps, with a desirably high degree of light output (90% and higher). This same problem, in a somewhat different situation in the turbidity evolution in opal glasses like a lead borosilicate glass, is met by an addition of $CaSO_4$ as the mineralizing and initiating agent.[93] When the glass contains about 2.5% F, the addition of $CaSO_4$ distinctly reduces the losses of F by volatilization. On the phase equilibria and liquid immiscibility in the system $PbO-B_2O_3-SiO_2$, see the recent investigations made by D. W. Johnson and F. A. Hummel.[94]

559. Comparable results of the nucleation mineralizing effects of F-turbid opal glasses achieved by G. Paoletti and F. Glammanco[95] included very characteristic bell-shaped devitrification curves established by optical measurements of the turbidity; for coarser suspensions, the Rayleigh-Gans approximations could be verified.[96] Interesting is the appearance of a compound of *xonotlite*, $6CaO \cdot 6SiO_2 \cdot Ca(OH)_2$ type, only with substitution of OH^- groups by F^- anions. The crystallization curves in the temperature range from 725° up to 846°C show a maximum of crystal growth at 750° to 800°C which is of equally great significance for those studies.

560. Highly valuable information is presented in studies made by H. W. Hennicke and H. Salge[97] on a commercial fluorosilicate opal glass, through the careful application of sodium silicate in the range from 50 to 85 mole % SiO_2, combined with NaF and CaF_2. The differential-thermal analysis and X-ray diffraction data are interpreted in combination with the results of systematic thermal treatments, and optical and electron microscopy, which make evident the unmixing reactions in the intermediate state before nucleation and crystallization. There is no doubt that the droplets suspended in a silica-enriched matrix glass must be relatively high in NaF and

[92] Proc. Symp. Coloured Glass, Czechoslov. Scient.-Tech. Soc. Silicate Industry, Prague, 1967, pp. 343–358.

[93] Cf. A. I. Neĭkh and M. A. Tsaritsyn, *Steklo Keram.* **23** (7/8), 419 f. (1966) (Engl. transl, *Glass Ceram. (USSR)*, Consult. Bur.).

[94] *J. Amer. Ceram. Soc.* **51**, (1968), (4), 196–201 (1968).

[95] *Verres Refract.* **23**, (6), 679–684 (1969).

[96] Cf. L. Prod'homme, *Rev. Opt. Theor. Instrum.* **45**, (4) 163–176 (1966).

[97] *Glastech. Ber.* **43**, (4) 138–146 (1970).

CaF_2 which are crystallizing as such, whereas silica (cristobalite) is formed only in the matrix phase.

561. X-ray diffraction techniques and electron microscopy were also basically applied in recent studies of an opalescent borosilicate glass by J. Jeanmaire,[98] with an oblong-shaped unmixing field in the ternary system $B_2O_3-Na_2O-SiO_2$, with a second particle population above 680°C, homogenized when heated above 780°C. Etching with dilute HF + HCl solution demonstrated that silica enrichment takes place in isolated spheres of the dropletlike unmixing products which grow isothermally at a speed in proportion to the cubic root of time (cf. Fig. 121). The experimental

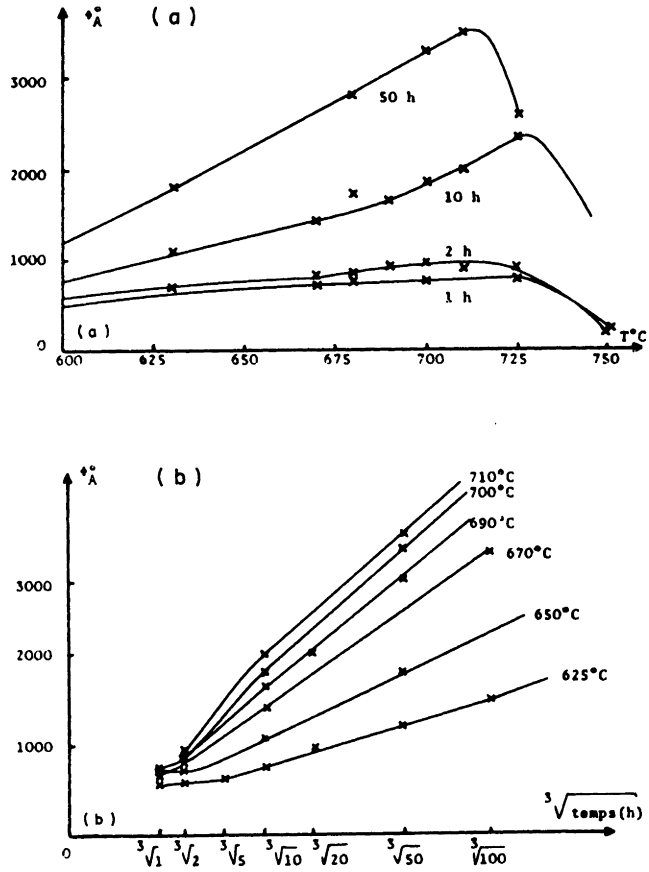


FIG. 121. Functional correlation of isochronous growth of spherical siliceous particles in opalescent Na borosilicate glass, (a) with temperature and (b) with time. (Jeanmaire.)

[98] *Verres Refract.* **24**, (1), 3–10 (1970).

results are in excellent agreement with the requirements of the Guinier–Fournet theory.[99]

OPALESCENCE AND TURBIDITY OF PHOSPHATE GLASSES

562. Before the reader goes further, it is urgently recommended that he become familiar with the crystallization products to be expected in glass compositions corresponding to complex phosphate minerals. The best introduction to recent investigations in this fascinating field is still the excellent book by J. R. van Wazer,[100] and also the recent comprehensive report by H. Wondratschek[101] on the crystalline phases of the *apatite-pyromorphite* family (on their crystal structures and isomorphism correlations cf. Vol. VI.A. ¶ 383–387). The definition of this highly important mineral type is to be made wider than it recently has been, since the apatites comprise not only the classical halogen (chiefly Cl^- ion) but also hydroxyl-containing species. Furthermore they comprise synthetic phases of oxypyromorphite $Pb_{10}[PO_4]_6O$ types, and are very stable and easily crystallize in synthetic products. In the compound $Pb_5[PO_4]_2[SiO_4]$ (silicoapatite) no halogen or oxygen anions appear but there is a doubling of the crystallographic parameter c_0.[102]

563. Typical *opal phosphate* glasses were prepared and studied by C. R. Das[103] in a series of glass compositions, systematically changed from common alkali CaO-aluminosilicate glasses (containing about 4% F_2 as a minimum) by substitution of Na_2O by P_2O_5; it is a practical experience that the ratio Na_2O/P_2O_5 is very important for the successful and reproducible manufacture of "milk glass." With increasing P_2O_5 introduction, such glasses evolve an increasing intensity of turbidity, measured as the percentage of light transmission. Increase in turbidity is even intensified by addition of CaO and BaO, both substituting for Na_2O. An optimum in turbidity is reached when P_2O_5 and alkaline earths are combined to form the monophosphates. Even still stronger opalizing effects are exerted by partial exchange of Al_2O_3 with alkaline earths; Al_2O_3 is assumed to exert a favorable influence on the melting, while ZnO and F_2 increase the homogenization of the turbid glass. Experimental investigations made also by C. E. Das[103a] illustrate (1) the

[99] Cf. A. Guinier and G. Fournet, "Small Angle Scattering of X-Rays," Chapter IV, Wiley, New York, 1955, (cf. VII. ¶ 352, 369).

[100] "Phosphorus and its Compounds," Vol. 1, Interscience Publs. New York, 1958.

[101] *N. Jahrb. Mineral. Abh.* **99**, (2), 113–160 (1963).

[102] S.a.H. H. Paetsch and A. Dietzel, *Glastech. Ber.* **29**, (9), 345–356 (1956), on the system PbO–P_2O_5–SiO_2 (cf. III.B. ¶ 444).

[103] *Cent. Glass Ceram. Res. Inst. Bull.* (*Calcutta*) **11**, (3), 68–71 (1964); **13**, (4), 101–107 (1966).

[103a] See Ref. 103, **14**, (3), 85–93 (1967).

substitution of silica by P_2O_5, (2) other replacements in the system $Na_2O-B_2O_3-SiO_2-P_2O_5$ by alkalies, alkaline earth oxides, and alumina, and (3) the functional influence of those modifications of composition on the degree of turbidity of the resulting glass products. It is interesting that the ratio Na_2O/P_2O_5 is again a particularly strong factor in the evolution of turbidity, in every case stronger than the ratio CaO/P_2O_5, whereas, MgO has a pronouncedly unfavorable influence. The crystalline phases as the origin of the opacity effect are Na tripolyphosphate, and/or Na pyrophosphate, in the presence of CaO or of Na – Ca orthophosphate. Unlike the flourine opal glasses, the opacity of phosphate opal glasses is stable with respect to time and temperature, but glasses without alkaline earth oxides even lose a certain amount of their opacity by annealing.[104]

564. More from the practical standpoint of the changes that take place in phosphate glasses during the *rolling* process (in manufacture of lining plates), P. Schleifer and Eliz. Rykiert[105] systematically used the X-ray diffraction method, the optical microscopic mineral identification methods, differential-thermal analysis, measurements of transmissivity (for the short wavelengths range specifically), and electric resistance. During the rolling, the share in crystalline phases increased markedly, and several new formations were observed. The endeavors were successful in finding out optimum conditions for the thermal treatment and a reliable reproducibility of desirable degrees of turbidity.

565. Aluminosilicophosphate glasses of the systems $RO-Al_2O_3-SiO_2-P_2O_5$ (with R = Be, Mg, Zn, Mn^{2+}) were systematically studied by R. Ya. Berzin', Ya. A Vaĭvad, and U. Ya. Sedmalis.[106] Other investigations made by U. Ya. Sedmalis, R. K. Shvinka, and Yu. Ya. Eĭduk[107] on the system $Li_2O-Al_2O_3-SiO_2-P_2O_5$ from the ternary partial system $Li_2O-Al_2O_3-SiO_2$, which is particularly important for the correct composition and the technology of glass-ceramics compositions in the ratio 1:1:8 corresponding to the mineral petalite, nevertheless, did not show in their microheterogeneous texture the crystallization of this type. Crystallite size and crystal growth is entirely dependent on the P_2O_5 content in the same way as it exerts controlling influence on the successful performance of the glass-ceramics manufacturing process. Sedmalis, Shvinka, and Eĭduk[108] examined the system $Na_2O-Al_2O_3-SiO_2-P_2O_5$ under the same aspects. Glasses with 30 wt. % Na_2O

[104] On the structure characteristics of crystalline phosphates, see also F. Liebau, *Angew. Chem.* **75**, (15), 735 (1963) (VI.A. ¶ 380).

[105] *Szkło Ceram.* **17**, (5), 113–115 (1966).

[106] *Izv. Akad. Nauk Latv. SSSR Ser. Khim.* (1), 46–49 (1966).

[107] In the book "Glass-forming Systems and Materials", (Yu. Ya. Eĭduk, ed.), pp. 145–150, Zinatne, Riga, 1967.

[108] Reference 107, pp. 169–178 (1900).

have, for compositions high in P_2O_5, a remarkably low viscosity and softening temperature; other glasses with only 20 wt. % Na_2O are suitable for the manufacture of *glazes* to be applied on ceramics with a particularly dense and fine-granular texture. When the ratio Al_2O_3/P_2O_5 is above 1.0, the compound $AlPO_4$, with a quartz-like structure and properties, is most probably present.

566. K. K. Karlson, U. Ya. Sedmalis, and Yu. Ya. Eĭduk[109] reviewed the evolution of alkali aluminophosphosilicate glasses from *natural* raw materials of the quinary systems $CaO-MgO-Al_2O_3-SiO_2-P_2O_5$,[110] namely, apatite, kaolin, dolomite, and a 10% addition of spodumene. The introduction of only 0.8% Li_2O is without any markable influence on the homogeneous crystallization behavior of the glasses in the basic quinary system; they have no trace of turbidity and opalescence, and on the other hand, the introduction of less than 1.5% Li_2O improves the fusion and homogeneity of the glass products.

567. Z. M. Syritskaya and S. A. Feĭkner[111] describe glasses of a high transmissivity in the near infrared of the spectrum, with a flat maximum for λ = 1.0 to 2.5 μ, and a rapid slope to low transmissivities for λ = 2.8 μ. It is particularly interesting that additions of TiO_2 to such aluminophosphatosilicate compositions bring about considerable improvement in the chemical durability of the ternary glasses, but only slight modifications in the near-infrared spectrum. Effects of an analogous type were observed with additions of BaO and WoO_3 to the aluminosilicophosphates, although in the latter complex glasses the introduction of hydroxyl groups is distinctly indicated by the absorption band near 2.8 to 2.9 μ.

568. J. M. Eldridge and P. Balk[112] demonstrated how, by the reaction of silica with vapors of P_2O_5 over a temperature range from 800° to 1200°C and several orders of magnitude for the effective vapor pressure of P_2O_5, one may prepare very thin films of phosphatosilicate glasses. The reaction is ruled by the solubility of tridymite in the liquid phase near, or on, the liquidus curve in the phase equilibrium diagram $P_2O_5-SiO_2$ (Fig. 122) after F. A. Hummel and T. Y. Tien (cf. Vol. III.B. ¶ 434, Author's footnote). Such glass formations with the participation of gaseous reagents are not restricted to building-up of phosphatosilicate glasses. In principle, the same reactions are observed in the formation of borosilicate glass films by the reaction of silica with, volatilzed B_2O_3; the same kinetic and thermo-

[109] In the book "Glassy Systems and Materials" (Yu. Ya. Eĭduk, ed.), 109–112, Zinatne, Riga, 1967.

[110] Cf. R. Ya. Berzin', O. K. Kukur, and K. K. Karlson, Izv. Nauk Akad. Lat. SSSR **4**, 399 ff. (1963); T. Kanazawa, *J. Chem. Ind. Soc. Jap.* **63**, (3), 477, A.24 (1963).

[111] In the book "Glassy Systems and Materials", (ed. Yu. Ya. Eĭduk), Riga 1967, Publ. Organ. Zinatne; **11**, 235–243.

[112] *Trans. AIME* **242**, (3), 539–545 (1968).

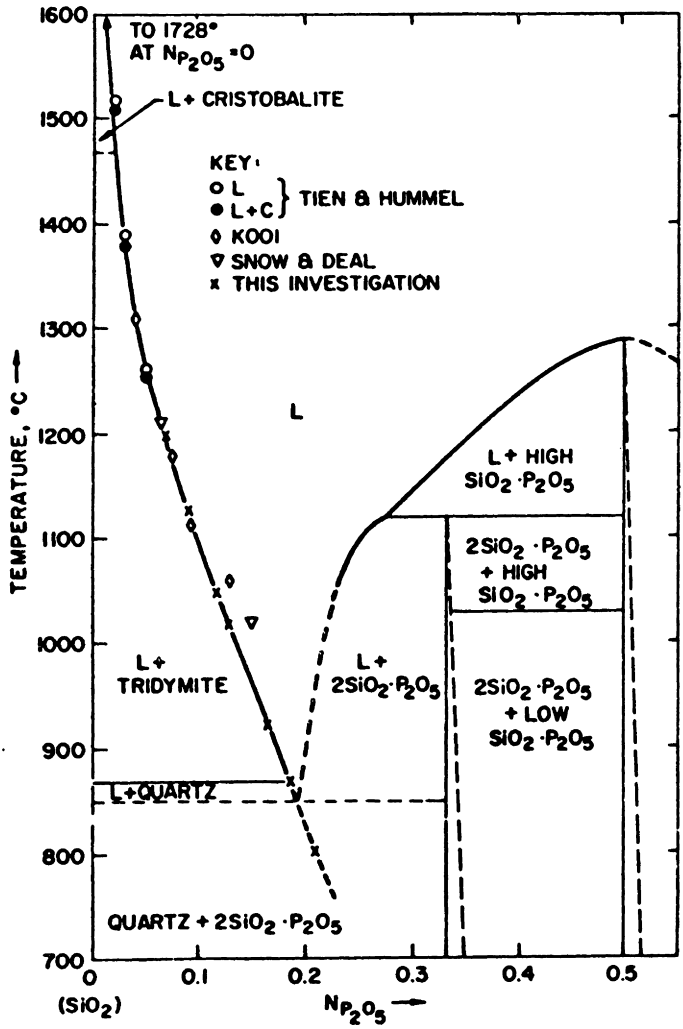


FIG. 122. Correspondence of phosphate–silicate glass compositions in the system $SiO_2-P_2O_5$ (after Tien and Hummel, 1962), with the maximum solubility of crystalline silica in the melt solution. (Eldridge and Balk.)

dynamic principles apply for the reaction mechanisms. Normally, such films have a thickness from 1000 to 8000 Å; as the reactive agent for P_2O_5, one may introduce $POCl_3$ in the place of silica glass, one may apply oxidized surface of elementary silicon, usually as a monocrystal of Si, as the substratum, thus creating a phosphato-silicate glass *in situ*. The vapors of P_2O_5, $POCl_3$, and related reagents are best introduced into the reaction chamber by a current of nitrogen. The method here

indicated is of great importance in electronics industry for FET devices,[113] especially for the surface stabilization of semiconductor-metal oxide capacitors and field effect transistors.

569. The often-described hydrolysis of $NaPO_3$ and of other Na phosphates in the presence of NaF at elevated temperatures, as an important factor in phosphate glass production or other technological processes, was recently studied by W. Franke.[114] When $NaPO_3$ is heated with NaF in dry air atmosphere, POF_3 is evolved and volatilized; in the residue are found (besides residual $NaPO_3$) $Na_5P_3O_{10}$ and $Na_4P_2O_7$, but not the double saltlike $NaF \cdot Na_3PO_4$. Glassy $NaPO_3$ is found with an end composition of 52 mole % $NaPO_3$, 48 mole % $Na_5P_3O_{10}$. Na phosphates may be used as a substitute for salt in making the well-known *salt glazes* for coating such common ceramic ware as heavy clay products and "basalt" ceramics, as is often discussed.[115]

570. As a supplement to the studies on *apatite* phosphates, we may remark that an "apatitelike" hexagonal modification of the simple lead orthophosphate $Pb_3(PO_4)_2$, does *not* exist, although literature on this problem might seem to confirm this incorrect hypothesis[116] as do the critical investigations made by U. Keppler;[117] most evidently, confusion with the oxypyromorphite phase did commonly occur when precipitation from alkali-containing aqueous solutions had been used (cf. L. Merker and H. Wondratschek, footnote 116).

TITANIUM DIOXIDE, ZIRCONIUM DIOXIDE, AND OTHER DIOXIDES IN OPAL GLASSES

571. G. Bayer and W. Hoffmann[118] studied with methods of electron microscopy the extension of TiO_2 nucleation and of unmixing ranges in the ternary system $Na_2O-TiO_2-SiO_2$ over a temperature range from the liquidus boundary curves to the transformation points, by the classical transmission and replica techniques,

[113] Cf. E. H. Snow and B. C. Deal, *J. Electrochem. Soc.* **113**, (3), 263–269 (1966).

[114] *Glastech. Ber.* **43**, (6), 234–236 (1970).

[115] E.g., by J. R. van Wazer in his book, "Industrial Chemistry and Technology of Phosphorus and Phosphorus Compounds," Wiley-Interscience, New York, 1958; further E. Tauber, D. N. Crook, and M. J. Murray, "Phosphate as a Substitute for Salt in Glazing," Rep. No. C.T. 1, 1971, Division of Buildg. Res., Commonwealth Sci. Ind. Res. Organztn. Australia, 1971, with an interesting "Gloss Diagram" in the system of different Na phosphates of industrial brands, e.g., for glazed roofing tiles. New regulation of Australia forbids, for ecological reasons, any use of salt glazing.

[116] Cf. L. Merker and H. Wondratschek, *Z. Anorg. Chem.* **306**, (1), 25–29 (1960), specifically p. 28.

[117] *Ber. Deut. Keram. Ges.* **46**, (5), 244–246 (1969) (cf. III.B. ¶ 444, 447).

[118] *Fortschr. Miner.* **42**, (1966), (2), 22 (1944); *Glastechn. Ber.* **39**, (8), 242–261 (1966); *Glass Technol.* **7**, (3), 94–97 (1966).

combined with the thin-etching method first developed for the structure of semiconductor systems (cf. Vol. VI.C. ¶ 194 ff.). It makes directly possible electron diffraction analysis of crystallization products in opalescent and turbid glasses. The special system $Na_2O-TiO_2-SiO_2$ is characterized by a wide extension of the concentration field of primarily crystallized sodium titanates in the immiscibility areas high in TiO_2. The electron micrographs show that the chief crystallization is initiated by heterogeneous mucleation on the phase boundaries of the unmixing fields. The powerful nucleator action of TiO_2 in glass melts is the basis of its wide application as an initiator agent for glass-ceramics ("Sitall" is the Russian word for these); we refer to Vol. III.A. 39 ff. and to special reviews presented by B. G. Varshal, N. M. Pavlushkin, and R. Ya. Khodakovskaya.[119]

572. G. Bayer's and W. Hoffmann's studies in the system $Na_2O-TiO_2-SiO_2$ and their turbidity phenomena show a very distinct effect of the viscosity as a function of temperature of the glasses by the observation of the Tyndall effect in relation to controlled annealing conditions over a range from 675° to 800°C. Fine-powdered glass samples crystallize much more rapidly than do massive fragments. Particularly important were direct observations of the crystallization of high-quartz and narsarsukite, $Na_2O \cdot TiO_2 \cdot 4SiO_2$, associated with simple titanates like $Na_2O \cdot 2TiO_2$; $Na_2O \cdot TiO_2$; rutile, anatase, and cristobalite, but also $Na_2O \cdot SiO_2 \cdot TiO_2$, in two modifications,[120] along with a few unknown phases, including "Na-titanate bronzes," type formula $Na_2O \cdot TiO \cdot (TiO_2)_x$ with $x = 7$ to 10, and 11 to 15 (metastable and disappearing at higher temperatures) which necessarily are connected with the presence of trivalent titanium (identified by nuclear paramagnetic and spin resonance measurements). Characteristic of these "bronzes" is a deep-blue-violet staining. Even more peculiar are brown colors appearing at higher temperatures.

573. R. Katzschmann[121] extended experimental techniques and studies to barium borosilicate glasses in which 10 and 20 wt % BaO were substituted by La_2O_3 and ThO_2. In these cases, the primary crystallization was measured by the temperature gradient method of O. H. Grauer and E. H. Hamilton (cf. ¶ 413, 542; Vol. II.B. ¶ 210). Liquidus temperatures were measured for glasses with the molecular ratio La_2O_3: ThO_2 = 1:1. When Al_2O_3 (about 1%) is added, this can be done to homogeneity only very restrictedly for achieving Crown glasses on the basis of Ba borosilicates containing La or Th oxide, with a high stability to spontaneous crystallization

[119] *Soobshch. Pyat.-go Vses. Soveshch. Sostoyan. steklyann. Tela; Leningrad* May, 1969; abstr. *Glastech. Ber.* **43**, (2), 59 f. (1970), including the unmixing phenomena in the course of crystallization of glass ceramics.

[120] Cf. O. K. Botvinkin and M. L. Mironova, *Vses. Nauch. Issled. Inst. Stekla* **10**, 14–23 (1957).

[121] *Glass Technol.* **6**, 156–160 (1965).

of these oxides; increasing alumina addition first reduces the maximum rate of crystallization, but then increases it, although in the same time the liquidus temperatures are reduced.[122]

574. Complex Ca titanosilicate glasses were examined in their electric conductivity by V. S. Molchanov, R. L. Myuller, and A. A. Pronkin,[123] as a paradigma for a general rule that the introduction of a new component to a simple alkali silicate glass causes increasing conductivity. The activation energy of conductivity of the alkali ions is, in this case, reduced when polar structural elements of divalent metals (e.g., Pb^{2+}) are replaced by less polar ones (preferably by Ti^{4+}). In this respect, previous observations by C. K. Russell, C. G. Bergeron, and A. L. Friedberg[124] on the crystallization of $CaTiO_3$ (perovskite) from TiO_2-containing Pb silicate and borosilicate glasses were made during cooling. Differential-thermal analysis and microscopic measurements of nucleation and crystal growth were made to consider that the temperatures of the exothermic peaks on those curves cannot coincide exactly with those of the crystallization rate, since the first case is based on a pure mass effect, whereas in the second case, the maxima are practically independent of the number of primary nuclei. Pb borate crystals which were also observed in these same experimental glasses show a considerable increase in crystallization speed when they grow in an electric (ac or dc) field; no corresponding reaction was observed for lead titanates.

575. Crystalline phases in glasses of the system $Li_2O-CeO_2(CeO_{1.5})-SiO_2$ were investigated by G. Bayer, J. Felsche, and W. Hirsiger[125] by solid-state reaction and full fusion, with a maximum CeO_2 content of 15 mole% for a completely homogenous glass. Among the crystallization products are the highly interesting Ce^{3+} silicates $Ce_2Si_2O_7$, and a new phase of ceroorthosilicate composition and apatite-type structures (cf. Vol. III.B. ¶ 137).

576. The numerous correlations between the mechanisms of *unmixing* reactions in molten glass, and those of *nucleation* and ensuing crystallization phenomena are of great technological significance as was disclosed in an extensive publication by G. Geirnaert.[126] The theoretical basis is given in derivations of a complete theory of thermodynamic "ripening" by I. M. Lifshits, V. V. Slyuzov (1961), and C. Wagner (1961) and the theory of "coalition" by J. Zarzycki and F. Naudin, 1967,[127] and even

[122] Cf. Y. Baskin, Y. Harada, and J. H. Handwerk, *J. Amer. Ceram. Soc.* **44**, (9), 456–459 (1961).

[123] *Solid State Chem.* pp. 101–104 (1966).

[124] Office of Techn. Servs. VI. 1963, Summary Rep. No. 3. AEC Contract No. AT (11–1) 915; abstr. *Glastech. Ber.* **40**, (8), 315 (1967).

[125] *Glastech. Ber.* **42**, (8), 317–321 (1959))cf. VII. ¶ 776).

[126] *Verres Refract.* **25**, (1), 21–30 (1971); **25**, (2), 81–86 (1971).

[127] *Phys. Chem. Glasses* **8**, (1), 11–18 (1967).

more recently by W. Haller, D. D. Blackburn, and F. E. Charles,[128] starting from the model system $PbO-B_2O_3$, and using low-angle X-ray diffraction methods. Typically, "milky" glasses of the system $Na_2O-Al_2O_3-SiO_2$ have, according to Geirnaert, a maximum of mechanical resistivity as a function of the time period of turbidity evolution. Pressure is inherent in the industrial shaping processes on the glass surface, both with the boundary zones of the glass "gob" in contact with the metal wall of the blowing molds and with the plunger which is rapidly cooled in the automatic machine.

577. The electron microscopy discloses local surface defects, crystalline nuclei,[129] or foreign particles ("dust") deposited during the pressing process, or development of cracks following the Griffith principles.[130] Structural differences between surface portions and the inner textures of a ZnO- and TiO_2-containing Na borosilicate glass were studied by transmission electron microscopy and carbon replica techniques of glass particles of a fine glass powder, also the appearance of unmixing droplets with indications of liquid flow and coalescence, in extensive statistical evaluation (by iteration methods). Particularly interesting in this respect are three-liquid phase immiscibility phenomena and nucleation, as seen in the light of the theory of W. Haller and M. Jeanmaire. Most striking here are enrichments in heavy elements like Zn and Ti in the unmixed droplets relative to the more transmittant matrix glass portions. The latter glass phase is enriched in Na borates; larger domains, however, are enriched in silica, just the contrary of what is observed in the unmixing of common alkali borosilicate glass.[131] Coalescence of the glass droplets sometimes surprisingly resembles that observed by R. Warren[132] in the system NbC–Co.

GLASS-TYPE PROPERTIES OF ENAMELS

578. P. Dekker[133] presented a wealth of experimental material and numerical data on the viscosity of "porcelain enamels," as a function of temperature, when determined by the classical and still thoroughly popular flow-button method of testing. The flow speed of the liquified enamel on an inclined plane plate measured here[134] is tentatively sufficient when combined with coordinates of composition

[128] *J. Amer. Ceram. Soc.* **53**, (1), 34–39 (1970).

[129] Cf. G. C. Kuczynski and J. Herbert, *Verres Refract.* **23**, (6), 675–678 (1969).

[130] Cf. F. M. Ernsberger, in *Progr. Ceram. Sci.* (ed. J. E. Burke), **3**, 57–76 (1963).

[131] Cf. W. Vogel (*Silikattechnik* **9**, (2), 51–62) (1958), and M. Jeanmaire, ¶ 561.

[132] *J. Mater. Sci.* (3) 471 f. (1968).

[133] *J. Amer. Ceram. Soc.* **48**, (6), 319–327 (1965); see also *Mitt. Ver. Deut. Emailfachleute* **11**, (4), 23–35 (1963), with a rich literature and publication reference on p. 327.

[134] On a correlation to more accurate measurements of viscosity see VII. ¶ 180.

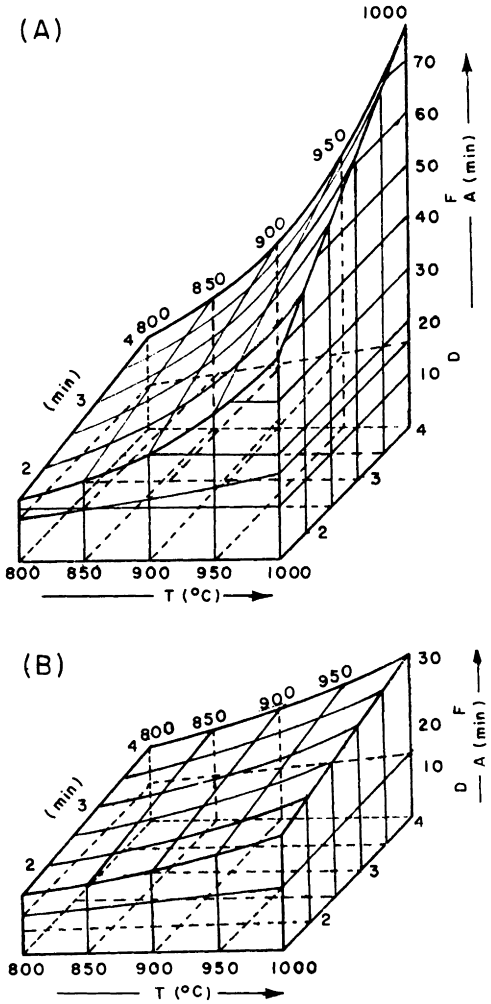


FIG. 123. Partial flow diagram and total distance curves, (A) for zirconia enamel powder and (B) wet titania enamel. (Dekker.)

and other properties in three-dimensional diagrams of which we give examples in Figs. 123 and 124, for TiO_2- and ZrO_2-turbidified powder enamels, together with a diagram for determination of the softening point temperatures from the strain curve using the derivation after W. Steger.[135] Figure 125 also shows the correlation between the flow rate, V, and viscosity (in mm/minutes) which is the basis for a very

[135] Cf. P. Dekker, *Mitt. Ver. Deut. Emailfachleute* **8**, (10), 71–80 (1960).

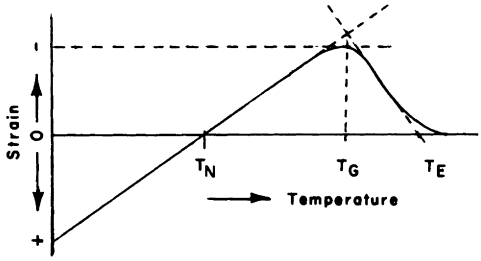


FIG. 124. Diagram for the determination of softening points from the strain curve according to Steger's method; T_N is the neutral point, T_g the transformation point, T_E the softening or strain point temperatures. (Dekker.)

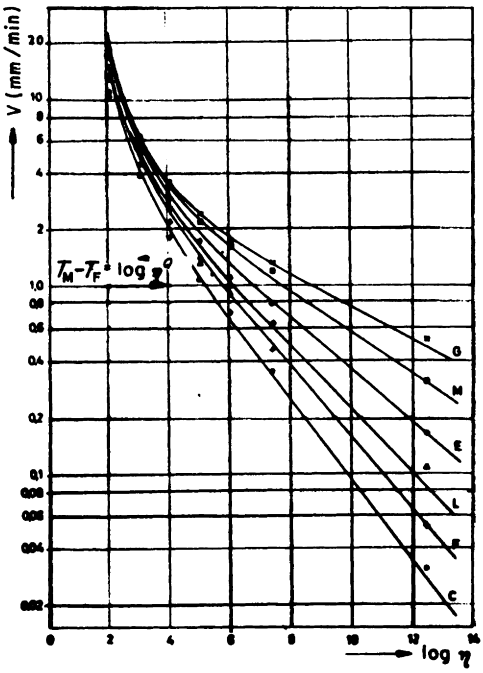


FIG. 125. Correlation of the flow rate V and viscosity η. (Dekker.)

simple but reliable practical method for a current control of industrial enamels of very diverse composition types and applications. We agree with the author that a full understanding of what the button-flow test is able to offer deserves greater attention than has been accorded it thus far.

579. Directed from equally practical viewpoints, are the observations of R. Krannich,[136] encouraging the use of quite modern methods for application of enamels onto metal substrata (steel sheets are the most common ones), with *electrophoretic spraying* of a liquid suspension and ensuing coagulation; on the dispersoid-theoretical basis of this method cf. Vol. VI.C. ¶ 88, 613, with application of special electrolyte deflocculents like bentonite, cellulose, "Zellin," alginates, tragacanth, gum arabic, and the like. Degreasing by alkaline rinsing and pickling with dilute HCl solution of the metal sheets must precede the spraying with semiconductor–(Si–) rectified direct current (voltage between 30 and 150 V). A very accurate control of temperature and conductance of the batch must be maintained for optimum conditions of the electrophoretic spraying of the slurry to produce a uniform thickness of the enamel layer. Control of aging pehomena of the suspensions must not be omitted to keep the solid content of the suspensions as constant as possible.

580. A. Petzold and M. Hübscher[137] discussed the effects of slight contaminations of glass enamels caused by divalent and trivalent iron in the raw materials, frits, and enamel bodies, respectively, which sensitively control the fusion and liquefaction conditions. One may transfer, nevertheless, many practically determined data for common glasses to enamels from more complex compositions; practically useful rapid control is, for instance, the indentation hardness test results which indicate changes in FeO content in the flows considerably more rapidly than one would expect from the same fluxes up to a total Fe content of 1.5 wt. %. Practically important also are the softening and transformation point temperatures of enamels with a total Fe content up to 1 wt. %.

581. Prestressed glassy enamel applied onto sheet glass was the subject of investigations by A. G. Shabonov, V. D. Churikov, and Yu. M. Tyurin.[138] Nowadays, its industrial importance for construction purposes equals that for production of safety glass windows in the automobile industry. In order to compensate deformation stresses building-up during application of enamel to glass, one may apply asymmetrical heating up and cooling schedules which require very high degrees of engineering skill and control to keep within the specification limits—the upper limit of 2 mm for warping over a length of 1 m.; as a rule, the thinner the glass layer, the stronger the deformation. For the observation of such critical requirements, the construction of special two-chamber kilns had to be developed for accurately controled asymmetric heating and cooling for windows up to 1500 × 2500 mm dimensions.

[136] *Silikattechnik* **18**, (9), 290–296 (1967); **18**; (11), 354–357 (1967).
[137] *Glas Email Keramo Tech.* **19**, (5), 153–157 (1968).
[138] *Steklo Keram.* **25**, (7/8), 395–397 (1968) (Engl. transl.).

Special low temperature ground-coat porcelain enamels of the system $Na_2O-B_2O_3-SiO_2-CaF_2$ have been developed and examined in their physical and chemical properties by M. A. Matveev[139] *in extenso*.

582. The *viscosity* of porcelain enamel frets was studied by R. A. Eppler and L. W. Smiser,[140] using a rotating cylindrical spindle viscosimeter of Brookfield type for $\eta = 10^2$ to 10^7 P; for higher viscosities ($\eta = 10^8$ to 10^{13} P) they observed the rate of deformation of a loaded beam; for highest viscosities ($\eta = 10^{13}$ to 10^{18} P) they used the beam-bending principle of this method.[141] To reduce thermal-expansion effects to a minimum, the entire furnace inner unit, the specimen support, and the "shepherd's crook" are of sapphire and high-density alumina refractory. With this experimental device and measuring procedure, a nearly ideal interpolation of viscosity over the whole useful temperature scale is made possible with a high correlation ($r = 0.978$) with the reciprocal of viscosity; thus, it could be concluded and demonstrated that surface-tension effects are of minimum importance in the fluidity behavior of enamels; at least they are insignificant with only 13% of the variation in fusion flow data ($r = 0.3621$); this result answers the question of whether the fusion flow (cf. the button test) measures the viscosity alone and not also a superimposed contribution from the surface tension.

583. Enamels for the chemical industry which are characterized by a better than normal resistance for acid and alkaline solutions are often prepared with additions of TiO_2 or ZrO_2, and must be for commonly used chemical laboratory glasses high in silica; such enamels, which are highly viscous at the temperatures postulated for the maturing process, are often blistered. (cf. footnote 141). A. Dietzel and H. J. Oel[142] followed the idea of introducing into suitable enamel-glass batches the noninert-gas-type cations of elements in the transition elements of the periodic system, i.e., Mn, Zn, Fe, Cu,[143] later of Ni, Co, Cd, and their mixtures. The enamels so developed show a desirable reduction in viscosity (relative to similar enamels with Ca and Mg), when those elements have more polarizability and improved chemical durability from the higher polarization effects exerted by oxygen anions. As a matter of fact, the correctness of theoretical considerations of this kind is confirmed by numerous experiments, starting with the systematically varied compositions of raw mixes, in respect to improved acid and alkaline brine resistivity and superiority over most of the enamels commonly available. A certain difficulty working against the expectations, however, is introduced by increased surface-tension parameters for the new

[139] *Vesci Akad. Nauk Belorussk. SSSR, Ser. Khim. Nauk*, (3), 41–47 (1968).

[140] *Bull. Amer. Ceram. Soc.* **47**, (8), 699–701 (1968).

[141] Cf. H. E. Hagy, *J. Amer. Ceram. Soc.* **46**, (2), 93–97 (1963); cf. VII. ¶ 149.

[142] *Mitt. Ver. Deut. Emailfachleute* **16**, (11), 81–85 (1968).

[143] Cf. A. Dietzel, L. Merker, and B.HAAS, *Sprechsaal* **95**, 414 f. 431–433 (1968).

types of enamels, which, however, may be compensated to a certain degree by the introduction of well-adapted intermediate enamel layers of common nature.

584. The important problems of the *wetting of ceramics* by *liquid metals*, and of wetting of metals by melts of enamels, were theoretically and experimentally studied by S. K. Rhee[144] in the reversed meaning, i.e., the parameters of the contact angle, and the temperature of a liquid-metal sessile drop resting on a ceramic substratum, as a frequently occurring problem of silicate technology. Concerning the work of adhesion, the effects of surface rugosity, porosity, and of chemical reactions, also structural changes in the surface of the substratum, are entirely analogous in their fundamental problems. We have listed only the general physical basis of those phenomena; the details discussed in Vol. VII. ¶ 179.[145] As a figurative paradigma consider the wetting conditions of alumina ceramics by liquid aluminum, and other metals[146] and some instructive systems taken from *Cermets* of molten metals/TiN, or TiC, or Ti borides, or Fe and Rh/HfO_2, for which it is not entirely excluded that eutectic reactions may occur between these constituents.[147]

ADHESION PROBLEMS OF ENAMELS ON METAL SUBSTRATE

585. A. Dietzel reported on the status of our knowledge of the adhesion reactions in 1963[148] on the same problem for metals/glasses and enamels.[149] For the interreactions between Fe metal and certain enamel compositions, P. P. Budnikov and V. A. Lyutsedarskiĭ[150] calculated the activation energy for such reactions at less than 10 kcal/mole, and reached the important conclusion that such interchanges are of purely diffusional character. This result is highly remarkable because it makes evident that such interchanges do not agree with essential chemical reaction mechan-

[144] *J. Amer. Ceram. Soc.* **54**, (7), 332–334 (1971).

[145] See also W. A. Zisman in the book "Contact Angle, Wettability, and Adhesion" (R. F. Gould, ed.), pp. 52–56, Amer. Chem. Soc., Washington, D. C. 1964.

[146] Cf. J. A. Champion, B. J. Keene, and J. M. Sillwood, *J. Mater. Sci.* **4**, (1), 39–49 (1969).

[147] Cf. C. R. Mannings and R. F. Stoops, *J. Amer. Ceram. Soc.* **51**, (8), 415–419 (1968), however, are inclined to discount this possibility; cf. II.C. ¶ 71, 92, on metal/slag systems; see also on the solubility of metals in glass melts by G. Gottardi and B. Locardi, *Vetro Silicati* **8**, (6), (48), 5–10 (1964); **12**, (5), (71), 5–8 (1968).

[148] *Mitt. Ver. Deut. Emailfachleute* **11**, (8), 71 f. (1963).

[149] A. Dietzel, Nina Köppen, W. Stegmaier, and E. Wegner, *DECHEMA Monogr.* **51**, 163–171 (1964), with a bibliography of older literature; on methods for microscopic investigation of porcelain enamels and a monograph of high practical importance in "Handbuch der Mikroskopie in der Technik" (H. Freund, ed.), Vo. IV, Section 4.

[150] *Dokl. Akad. Nauk S.S.S.R* **170**, 390–393 (1966).

isms, at least not in the degassing period of B- and B-free enamels. We will come back to this situation somewhat later in a different correlation.

586. A most instructive and comprehensive series of publications on the nature and reactions of so-called "adhesion oxides" from M. P. Borom and J. A. Pask[151] assembles their role in the development of chemical bonds at glass/metal interfaces, taking simple alkali disilicate melts as models for enamels, as studied by thermogravimetry, optical and electron microscopy, and electron-beam microprobe analysis. The general conclusion is that the adherence oxides change into alloys at the interface which tend to establish and maintain equilibria with the adjoining glass phase, at the same time enhancing oxidation of the metal substratum. The well-known crystallization of metal dendrites in the bulk glass and the "nickel flash" phenomena in the practice of porcelain enameling as described earlier by A. Dietzel and his school are now fully elucidated in such reaction sequences (cf. Vol. VII. ¶ 186, 273).

587. The physical-chemical principles for the discussion of metal/glass boundaries interfaces were briefly, but impressively, disclosed by Borom and Pask,[152] with the equilibrium conditions for a stable chemical bonding in contact zones. The glassy phase must be *saturated* with the low-valence oxide of the metal in question (or alloys). Redox reactions are typical of nonequilibria which tend to the true equilibrium state with all the ensuing consequences of the adhesion and resistivity of the bond strength. The thermodynamics of the activation energies for such reactions are the expression of possibilities for a quantitative calculation not only of the chemical reaction parameters, but also of adhesion and cohesion forces. Satisfactory adhesion and stability of chemical bonding as conditions for these parallel the contact angle of wetting, the determination of which converge to the zero value.

588. The initiation of such reactions on an electrochemical-thermodynamic basis, was again systematically presented by M. P. Borom and J. A. Pask in articles on reactions of iron, nickel, and cobalt, with simple glasses of Na_2O, $2SiO_2$ composition,[153] first for the diffusion kinetics in the different systems with disilicates having activation energies near 30.4 kcal/mole, later for their electrochemical significance concerning the electromotive forces of galvanic cells for the calculation of the redox reactions from chemical activity data (cf. Vol. VII. ¶ 186, 273).

589. Among newer publications of A. Dietzel *et al.* we mention one on the

[151] *J. Amer. Ceram. Soc.* **49**, (1), 1–6 (1966).

[152] Int. Glass Congr., 7th, Bruxelles, 1965, *C.r. Acad. Sci.* II. 3/81. 1–11 (1965); Rep-U.C.R.L.-11 816 Rev. AEC Contract No. W-7405 eng.-48, abstr. *Glastech. Ber.* **41**, (6), 259 (1968).

[153] *J. Amer. Ceram. Soc.* **50**, (2), 61–66 (1967), with J. A. Longwell, **51**, (9), 490–498 (1968); **53**, (10), 559–562 (1970); **53**, (12), 616–619 (1970); **54**, (5), 236–239 (1971), with A. M. Lacy.

adhesion mechanism for one-layer, direct-on techniques of enameling procedures,[154] and one on the effects of Co and Ni in the ground coats and direct-on white enameling processes[155]; more technological details on "fish scaling" and other defects common in such products will be discussed later (cf. ¶ 599 f.).

Chemical Interchanges between Metal Phase and Enamel Melts

590. We recall from ¶ 588 that now we have to speak on the possibility of an eutectic solubility relationship between metal surfaces, usually an iron (steel) sheet with a silicate melt or "enamel" in the widest meaning of the word. Simple alkali silicate melts are often used as models. In this understanding, V. Gottardi and L. Locardi[156] observed iron in contacts with sodium disilicate melts at 1200°C, first in pure argon atmosphere, then in an oxidizing gas surrounding. The amount of iron "dissolved" varies with the composition of the glass melts, particularly with the degree of impoverishment in alkali. Experimental variations were observed in the valence state of the dissolved Fe, and the rate of dissolution, as revealed by metallographic examination of the sheet surface after removal of the molten silicate. The interaction between both phases was therefore best interpreted as a process of charge exchange approaching certain states of equilibrium. The fact is finally established that iron cannot be dissolved without having been changed to ions, i.e., after some oxidation reaction.

591. This postulate, however, does not exclude the possibility that even in a pure argon atmosphere, dissolution of the metal occurs *indirectly* by transfer of positive charges from Na^+ ions by their reaction with $2e$, i.e., when Na is evaporated as the element, additional reactions like the following one occur:

$$Na^{2+} + \text{solid Fe (metal)} \rightarrow 2Na \text{ (in vapor)} + Fe^{2+}$$

At 1200°C the quantitative output of such a reaction between iron and $Na_2O.2SiO_2$ melt is much higher (see curve *A* in Fig. 126), namely, 98.0%, after 5 hours, than it is in pure argon atmosphere (curve *B* in Fig. 126), namely, 11.8% in the experiment; corresponding weight losses by evaporation of sodium are seen from Fig. 127. All of the iron ionized by the reaction is not necessarily in the divalent state and thus dissolved; the ratio FeO/Fe_2O_3 may vary from 99 to 98% FeO for the experiment with inert argon, but from 83% FeO initially to 12.5% when observed in an oxidizing atmosphere, as seen from the experimental data over a period from 1 to 5 hours (see

[154] Cf. *Mitt. Ver. Deut. Emailfachleute* **16**, (5), 27–31 (1968).
[155] *Mitt. Ver. Deut. Emailfachleute* **16**, (5), 55–57 (1968).
[156] *Vetro Silicati* **8**, (6), (48), 5–10 (1964).

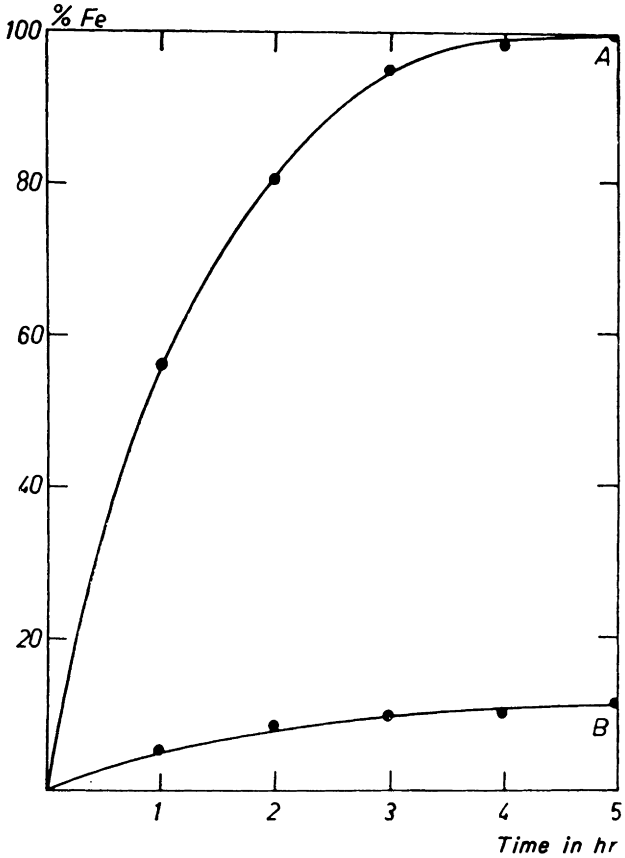


FIG. 126. Total iron dissolved in glass melt of composition $Na_2O,2SiO_2$, at variable times and constant temperature of 1200°C, Curve *A* for the melt system in oxygen atmosphere, curve *B* in argon. (Gottardi and Locardi.)

Fig. 128). Such results are highly conclusive for studies on the depth efficiency of those reactions over a profile from the surface of the metal to variable thicknesses of enamel layers on it. We must here omit a detailed discussion of problems of the progressive permeation of oxygen (in the oxides) into the micrographic structure of iron alloys in the system Fe—C, in view of the tremendous variations in the purity of industrial iron sheets. The well-known corrosion of crystallites from the boundaries follows well-defined crystallographic directions in the metal monocrystals.[157] New experimental data confirmed the stoichiometric equivalency of the

[157] See also the same authors, *Vetro Silicati* **12**, (5), (71), 5–8 (1968).

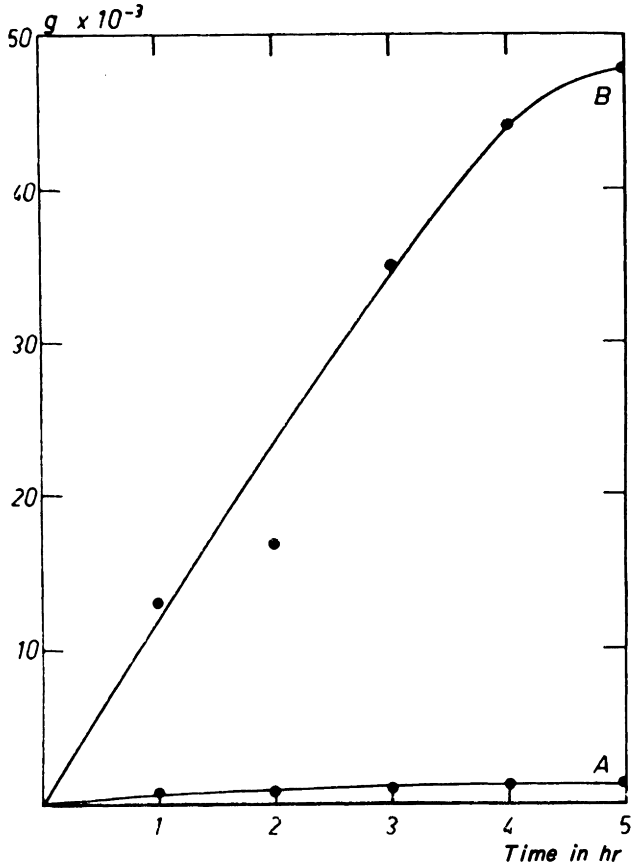


FIG. 127. Weight losses (in 10^{-3} g units) of Na_2O from 5 g of the glass of composition $Na_2O,2SiO_2$ (in curve *A*), and from the same glass, but containing 0.5 g FeO (curve *B*) as a function of time at constant temperature of 1200°C, in argon atmosphere. (Gottardi and Locardi.)

amounts in dissolved metal, and in volatilized alkali. The dissolution of nickel follows the same mechanisms but the reaction is much slower than with iron.

592. For the efficiency of steel sheet enameling two things of the highest importance are the immediate behavior of both solid/liquid phases in the presence of a more or less oxidizing surrounding atmosphere and the presence of *hydrogen* and its absorption mechanisms when (low-in-carbon) steels are dissolved in dilute acids. R. M. Hudson[158] studied these phenomena *in extenso* for corrosion of steel in dilute

[158] *Corrosion* **20**, (8), 245*t*–251*t* (1964).

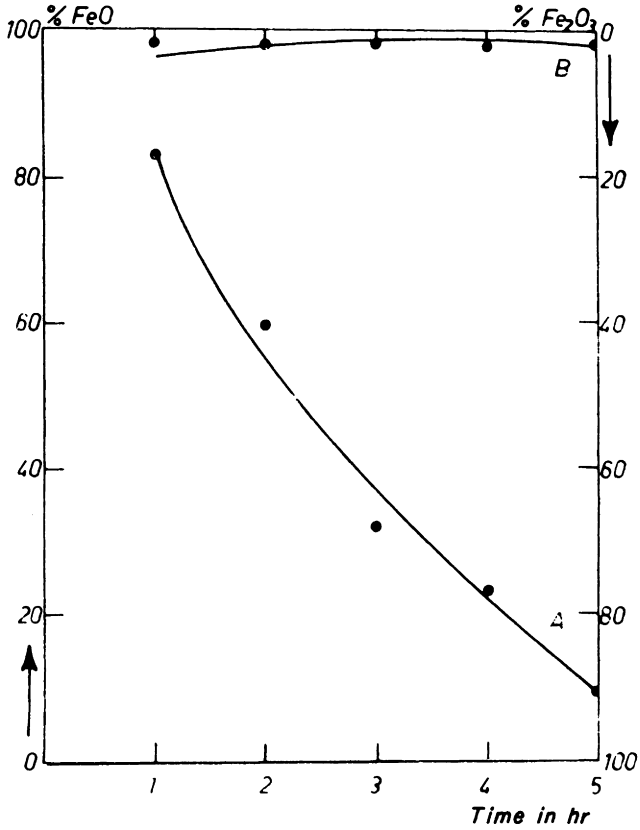


FIG. 128. The ratio FeO/Fe_2O_3 in the glasses of Fig. 126, but thermally treated in oxidizing atmosphere (curve *A*) and in argon (curve *B*), at 1200°C. (Gottardi and Locardi.)

HCl, H_2SO_4, H_3PO_4, and HNO_3. Quite specific rates of dissolution were found for the single acids in different normalities of concentrations. The amount of hydrogen introduced into a steel during dissolution in HNO_3 is much lower than it is for the other acids; the percentage of theoretically available hydrogen absorbed in steel after a given weight loss did not differ significantly among HCl, H_2SO_4, and H_3PO_4; the amount of hydrogen absorbed at a given weight loss decreased with increasing temperature. It is important that the chemical-metallographical and analytical composition of the different steel sheet qualities available in commerce be carefully studied and considered for these highly complex phenomena which are of vital interest for enamel practice.[159]

[159] Cf. H. Bablik, "Hot Dip Galvanizing," pp. 31–68, Wiley, New York, 1950.

593. Equally important among steel enameling practice conditions is the equilibrium of the "decarbonization" reaction

$$C\ (\text{in steel}) + H_2O \rightarrow CO + H_2$$

which rules the behavior in "wet" atmospheres. It was studied by R. M. Hudson, A. W. Abel, and G. L. Stragand,[160] as a function of temperature and the carbon content of the steel, over a technologically useful temperature range; and of C activity in Fe, relative to graphite in C concentrations ranging from 0.013 to 0.74%. The influence of cold reduction on the behavior of hydrogen in very pure iron was investigated by R. M. Hudson and K. F. Riedy.[161] An increase in hydrogen solubility (when "acid-charged") with increasing cold reduction was definitely established. This increase from 0 to 80% of cold reduction was much more pronounced, however, in lots of higher oxygen content. The pure iron lots were then subjected to conventional ground-coat *reboiling tests* in which material high in oxygen exhibited only a slight reboiling, whereas material low in oxygen showed heavier reboilings in some cases.

594. *Blistering* and reboiling phenomena in enamels and in *glazes*, are so closely related that their highly undesirable occurrence may be discussed from much the same aspects. Therefore, we mention H. Scholze's studies of blistering in *glazes*[162] with fascinating hypotheses and much information on solubility problems of gases in silicate melts in general, as in the apparently so elementary processes of "water" solubility in sodium silicate melts. Each individual blister is seeded from one "nucleus" center which most frequently is located in boundary layers (like metal/enamel melt, or ceramic body/glaze). This may be treated as a normal event in the technological processing, but it must be studied carefully with the most modern analytical methods, or even better, with gas chromatography and mass spectrometry. Such refined methods can yield totally meaningful results only if the bubbles are "frozen in" by temperature quenching, and if they are analyzed directly after their evolution.[163]

595. Another very important question of practical steel sheet enameling is that of the *permissible concentration of water vapor* in the kiln atmosphere, as discussed by A. Dietzel, H. O. Mulfinger, and M. Buck[164] in respect to defects in the enameled pro-

[160] *Trans. AIME* **232**, (5), 879–883 (1965); see also R. M. Hudson, *Trans. AIME* **227**, (6), 695–699 (1963), on detais of the kinetics of this reaction.

[161] *J. Amer. Ceram. Soc.* **44**, (10), 467–471 (1961).

[162] *Ber. Deut. Keram. Ges.* **44**, (2), 59–63 (1967).

[163] Cf. R. Galanulis and H. Scholze, *Ber. Deut. Keram. Ges.* **44**, (11), 533–539 (1967); cf. ¶ 200, 203, for the experimental techniques, with great emphasis given to iron oxides for the evolution of gas bubbles, in general.

[164] *Mitt. Ver. Deut. Emailfachleute* **13**, (1), 1–7 (1965).

ducts not only be seeding and blistering, but by the well known "fish-scaling" phenomenon. The rate of cooling after enameling has considerable influence on this fault origin under the action of water vapor; the blisters appear in the maturing process during rapid cooling. The permissible water concentration shifts to lower concentration when the carbon content of the steel is increased. The influence of the fuel gas is also not to be overlooked; a gas type like propane makes a relatively small contribution of water to the combustion gas content. Common fuel gas from city and coke-oven gas plants is decidedly high in water content.

596. For *cast iron* enameling, V. G. Upadhyaya, H. O. Mulfinger, and A. Dietzel[165] used *gas chromatographic* methods for the determination of the gases derived from the cast iron *per se*, the enamel *per se*, and those originating during enameling. More than 90% is hydrogen; the gas evolved from cast iron; CO is a product of the solid-state reaction processes

$$FeO + C \rightarrow CO + Fe$$

and

$$CO_2 + C \rightarrow 2\ CO$$

when the partial pressures of CO and CO_2 are below 0.44. Moisture content of the air in which the cast iron is enameled increases formation of CO, and the ratio p_{H_2O}/P_{H_2} is below 0.596. When the cast iron is intensely scaling (oxidized), blisters are formed particularly easily. Many more observations and recommendations of great practical value are to be found in these comprehensive publications. In connection with these problems, reports on the so-called *hydrogen embrittlement* of metals by H. C. Rogers[166] may be cited because of their correlation with the *pickling* and *electroplating* processes often combined with enameling. The importance of technological defect investigations is emphasized by Rogers with numerous examples and a rich bibliography and reference literature (cf. Vol. II.C. ¶ 99).

597. Speaking of typical enameling *pickling* and *nickel-flashing* practice, we first emphasize the fascinating studies made by A. Raccanelli, E. Ramous, and G. Cevales[167] of the so-called "direct-on" enameling (cf. ¶ 589). These authors worked with electrochemical measurements of steel sheets (specially developed for the direct-on practice) to determine the influence of time and concentration fluctuations in Fe^{2+} in the liquid enamel on the contact surface boundaries with the metal. The authors conclude that the *nickel plating* process produces a uniform layer only in

[165] *Mitt. Ver. Deut. Emailfachleute* **15**, (6), 49–59 (1967).
[166] *Science* **159**, (3819), 1057–1064 (1968).
[167] *Vetro Silicati* **11**, (6), (66), 5–10 (1967).

the first phase, but soon becomes irregular within a quite definite time period. M. R. Hudson[168] investigated important time factors in pickling with HCl, which is required for hot-rolled steel strips (steel type *L*). An iron build-up in the bath causes an increase in the pickling time. The HCl vapor pressure is also an influence, particularly on short pickling times.[169]

Recent Progress in Advanced Enameling Processes

598. The problem of enameling *aluminum* metal sheets, which for a long period presented great difficulties, is practically solved. Special developments may be seen in a report by P. P. Budnikov, K. P. Azarov, and A. S. Migonadzhiev,[170] on development and application of *phosphate enamels*, of the system $Na_2O-Al_2O_3-B_2O_3-SiO_2-P_2O_5$ (with 10 to 20% Na_2O and B_2O_3, 10% Al_2O_3, and 40 to 50% P_2O_5). Additions of BaO, ZnO, and NaF increase the fluidity; CaO, MgO, and TiO_2 raise the softening temperatures of the enamels. Alumina influences the viscosity within certain limits and favors gas blistering that must be carefully controlled. Other oxides may correct, from case to case, the properties of the enamels and their activity, improving wetting on the aluminum metal and reducing the contact angle. The blistering is specifically worsened by the use of fluorides and Li_2O, which cause gas evolution on the contact surfaces of the enamel flux with the metal sheet. On the corresponding experimental results for the enameling of iron (steel) sheets by electrochemical reactions, see above the observations made by P. P. Budnikov and V. A. Lyutsedarskiĭ (cf. ¶ 585),[171] also with respect to specific adherence agents like Co and Ni oxides, all in full agreement with A. Dietzel's electrochemical theory of adherence phenomena.

599. Furthermore, it should be mentioned how A. Dietzel and his school developed and interpreted advanced methods of a one-layer or "direct-on" enameling, without any ground coats in enameling. First we cite as a general introduction into this highly interesting technological field a report by A. Dietzel,[172] then studies by H. O. Mulfinger and C. T. A. B. Haas[173] on systematic experiments with steel sheets based on the indispensable acid pretreatment called the pickling. Here, the most

[168] With C. J. Warning and D. W. Brown, *J. Metals*, March, 5 pp. of reprint, (1961).

[169] On the metallographic examination of acid-pickled L-MR steel, see more recently R. M. Hudson, W. E. Petrick, and C. J. Warning, *Mater. Protect.* **5**, (5), 52–56 (1966).

[170] Third Internatl. Congress on Porcelain Enamels, by C.I.P. Porcelain Enamel Centre, Milano, 1962, pp. 363–397; see also the book "Inorganic Materials," pp. 373–381, Izd. Nauka, Moscow, 1968.

[171] *Dokl. Akad. Nauk SSSR* **170**, 390–393 (1960).

[172] *Metalloberflaeche.* **21**, (12), 372–373 (1967).

[173] *Mitt. Ver. Deut. Emailfachleute* **18**, (13/14), 115–121 (1967), in continuation of the previous publication *ibid.* **18**, (7/8) 136–142 (1965); cf. ¶ 583, footnote 142 f.

important factor is evidently the chemical composition of a thin wetting surface layer on the sheet when chloride containing white enamels are to be applied which react with the carbon content of the steel in the indispensable presence of water. Pickling of steel sheets is strongly impeded if electrochemically "nobler" alloys are present in the reactive surface layer. We repeatedly emphasized in our text the determinative role of the presence of water in enamels, and do this again according to the experiments of Mulfinger and Haas which concern direct-on enamels relatively high in chlorides. When these were applied in a perfectly *dry* state, the enameling could be done immediately without any objectionable disturbances like blistering or "fish scaling." The noticable influence of the carbon content of steel sheets is then not much more than a side reaction phenomenon of CO and H_2 evolution by the reaction of carbon and water.

600. A. Dietzel[174] explained the mechanism of adherence for the single layer in direct-on enameling, by an increased nickel metal deposition with extended etching by the exposure of *copper* in steel sheets which undergoes a strong local bonding on the iron. When the copper content of the enamels is kept too low, the adherence is unsatisfactory; on the other hand, when the Cu content is too high it impedes the rate of etching (pickling), and the copper is deposited as small spheres on the surface of the sheet. Fishscaling, black spots, or other defects then appear in the enamel coating. The manner in which the nickel is precipitated onto the steel sheet may be varied. It may be deposited by immediate galvanic action or, better, without any participation of direct current simply by addition of strong reducing agents like Na hypophosphite or, again, by the commonly known *dipping* process from a solution of nickel sulfate. It is only essential that a minimum amount, say 2 g/m^2 nickel is deposited, by the simple measure of the potential effect Fe/Ni of 0.20 V. Increased rugosity of the sheet surface, achieved by a deep etching in pickling before the Ni dipping, is suggested in the instructions given by a German patent application[175] to use the so-called "Beizbast" (a more or less loose residual aggregation observed in the baths for pickling) for improving the anchorage of the nickel particles on the roughened surface. Dietzel explains these observations as possibly only a mechanical effect of residual cementite, Fe_3C, accumulating as crystalline particles during the etching of steel sheets. This opinion is confirmed by X-ray diffraction diagrams of such residual material brushed from the sheet surface. Nevertheless, Dietzel is inclined to assume that the simultaneous precipitation of Cu and Ni will be, by far, more important for the final effect of the surface treatment as indicated; electron-beam microprobe determinations confirm this conclusion in concentration profiles for Ni and Cu across the steel–enamel surface.

[174] *Mitt. Ver. Deut. Emailfachleute* **16**, (5), 27–31 (1968).

[175] By Fr. Rickmann and O. Rappe, *K* 41, 889, VI.b/48c; see also Pat. 1,085,745 (1960).

601. How important the *quality* of the *steel sheets* chosen for the one-layer (direct-on) enameling process is for an optimum technological success was demonstrated by U. Held.[176] Preferably, open-hearth steel sheets, with a maximum C content of 0.10%, very low in Si, Al, Cr, P, and S, and of uniform pearlitic-ferritic texture should be used. The presence of grain boundary cementite is particularly undesirable. For quick control of presumable hydrogen behavior of the sheets, Held recommends a cathodic gas treatment by a direct current intensity of 50 mA/cm^2; for predicting tendencies of fish scaling, a simple observation of the time needed until the first bubbles of H_2 appear on the back side of the sheet will be sufficient (this test however, is not applicable to Ti-killed steels).

602. Easily flexible and electrically insulating coatings on steel sheet for special uses were developed by G. P. Sedmalis, U. Yu. Sedmalis, P. I. Vosilyus, and Yu. Ya. Eĭduk,[177] on the basis of the borophosphate systems $BaO-Ni_2O_3-$ and $SrO-Co_2O_3-B_2O_3-P_2O_5$, containing 20 wt. % of the alkaline earths, 10 to 25 wt. % R_2O_3, and up to 60 wt. % P_2O_5. The fusion temperature of such fluxes is only 750° to 800°C, for an optimum adhesion with the metal. When Al_2O_3 and SiO_2 substitute for a portion of the BaO and SrO, the modified enamel compositions show distinctly improved electric properties which make such products specifically suitable for insulating coatings.

603. One-layer (direct-on) enamels for steel pipe line tubings were developed to offset a shortage of raw materials and have been the aim of studies by Y. P. Liepin, Yu. Ya. Eĭduk, and P. G. Pauksh[178] utilizing mineral concentrates and slags from metallurgical processes for making Ti steels, or carbon-impoverished steels. The enamels resulting are aluminoborosilicates which, when first applied onto the metal, evolve gases, but in the maturing state, rapidly dissolve the oxidizing layer, spread uniformly, and thus develop an entirely even coating. Particularly important for the enamel composition is the choice of an Na–Ca borosilicate type, namely the eutectic of the system $Na_2O \cdot CaO \cdot SiO_2-Al_2O_3-B_2O_3$, and the addition of Fe and Ti, either from Ti steel wastes or from ilmenite concentrates.[179]

METAL-CERAMIC SEALING TECHNOLOGIES

604. In continuation of our discussions on the interactions between molten enamels and a metal substrate, we remember the important diffusion phenomena and

[176] *Silikattechnik* **20**, (3), 384–386 (1969).

[177] In the book "Vitreous Systems and Materials" (Yu. Ya. Eĭduk, ed.), pp. 253–257, Izdat. Zinatne Riga, 1967.

[178] See Ref. 177, pp. 259–265.

[179] Nepheline syenite; cf. Ya. P. Liepin', E. N. Podkletnov, and Yu. Ya. Eĭduk, Theses of the Scient.-Technol. Conference for Enamels and the Enameling of Metals, Izdat. Khimiya, Moscow and Leningrad, 1964.

their investigation in model systems of Fe, Co, Ni, with molten sodium disilicate.[180] Chs. A. Greenberg and R. L. Cook[181] extended such studies to PbO-containing borate enamels for a direct application on the sheet surfaces. When the fusion process takes place in air atmosphere, *metallic lead* is precipitated (visible in the electron micrographs as single droplets). When, however, the substratum on the borate enamel is applied to *copper* substratum, no such segregation of lead occurs. In this case the electron micrographs disclosed both lead spheres and lead borate. No iron borate, Fe_2FeBO_5, or fayalite could be observed, depending on the conditions changing from case to case. There is no typical band texture which might improve the adherence in the limits of the composition maintained in the experiments, and the corresponding temperature distribution. A real band structure with bands of lead metal 15–20 μ in thickness, as previously described by I. Buck,[182] and a layer of iron borate or silicate, with steel and a frit of Pb disilicate, were found. In the oxidation–reduction reaction, the PbO acts only as a "blanket" controlling the ionic state of the iron in the vitreous solution.

605. The important application of *metal alloy/glass* (or enamel) melts was emphasized in ¶ 385, after the investigations by P. J. Salt,[183] for example, of "NILO K" alloy and molybdenum/glass, molten in a high-frequency electric furnace. For the correct choice of both groups of metals, it is indispensable not only to determine the characteristics of thermal expansion; other equally important physical properties must be determined too. Oxidation of the metal is essential for a strong bonding effect on the contacts which is achieved and reproduced only under careful control of uniformity, and by reducing to a minimum possibilities for the formation of cracks. Accurate instructions are presented for correct control and preparation of the NILO K alloy, and of molybdenum, with all the variables influencing the properties of the enamel glass.

606. For "brazing" *oxide ceramics*, chiefly alumina and beryllia, onto metals, which is indispensable in modern electronic and tube rectifier cases, G. Schmidt[184] recommends special Fe, Co, and Ni alloys like "Nicosil 71" or "Vacon 70" and as solders Ag, Cu, and their alloys which may sometimes also contain Au, Ni, Sn, In, or Pd. In a so-called sinter-metal method, a hydrogen–oxygen flame sprays the surface of the ceramic body with a suspension of molybdenum in finest powder form, with oxides of Ti, Mn, or other fluxes, to form at 1250° to 1550°C a cover of sufficient adhesion strength. Another elegant method for an excellently adhesive layer, the

[180] Cf. M. P. Borom and J. A. Pask, *Phys. Chem. Glasses* **8**, (5), 194–202 (1967); *J. Amer. Ceram. Soc.* **51**, (9), 490–498 (1968): cf. VII. ¶ 186f.

[181] *J. Amer. Ceram. Soc.* **50**, (2), 84–90 (1967).

[182] *Bull. Amer. Ceram. Soc.* **32**, (4), 114–117 (1953).

[183] *Glass Technol.* **8**, (5), 127–130 (1967).

[184] *Silikattechnik* **18**, (7), 214–215 (1967).

so-called "active metal" method, requires application of titanium hydride in one soldering operation in a high-frequency vacuum furnace.[185]

607. Because of the great technological importance to the electronic industry of investigations of the adherence of metal layers hard-soldered onto ceramics, we have to discuss an instructive article by H. Rochow (cf. Vol. VII ¶ 185).[186] This author emphasizes the indispensable conditions for adhesion of the metal layers in "metallization" procedures on steatite ceramics, or on pure alumina, the correct control of chemical reactions between the ceramic surface and the metal melt, the good wettability of the substrate by filling-up of pores in the ceramic structures with those reaction melts, and the tight mechanical cohesion of both materials after solidification. An anchorage effect of acicular crystallites of the reaction products is, in this respect, particularly important. The fundamental systems for the metal-ceramic reactions which can fulfill these requirements are those of $FeO-Al_2O_3-SiO_2$ and $MnO-Al_2O_3-SiO_2$, and those of the titanate-forming systems with $FeTiO_3$, $MnTiO_3$, and $MgTiO_3$ as crystalline phases as observed in micrographs of hand-sealed samples of steatite with Fe–Mn alloys.

608. For alumina substrata in combination with Mn–Mo metal alloys, O. Kubaschewski and E. Evans[187] discussed the thermodynamic phase equilibria for the simplest metal oxides concerned here. Not only is the presence of hydrogen as the reducing atmosphere for such reactions most essential; the degree of moisture in this atmosphere must be taken into account as a variable as plotted in the curves indicating typical dewing point temperatures of the reaction gas phase (in the left-top portion of Fig. 129), which have been determined by J. Kotowski and J. Muschaweck.[188]

609. A sinter technique was described by R. M. Fulrath and E. L. Hollar[189] for the *soldering* of molybdenum-metallized ceramics with a manganese glass. For common ceramics a conventional method of maturing a mixture of molybdenum and manganese powders in an atmosphere of "moist" hydrogen, at 1500°C is sufficient. In this process an $MnO-Al_2O_3-SiO_2$ layer is built up which permeates the (mostly porous) ceramics and penetrates the metal by capillarity to develop a dense, mechanically durable sealing. When the ceramics are high in Al_2O_3, or the body is a silica-free glass, such coatings are not sufficiently durable under mechanical

[185] Cf. R. J. Bondley, in "Metal-Ceramic Brazed Seals" *Electronics* **20**, (10), 97–99 (1947), with silver at 1000°C.

[186] *Ber. Deut. Keram. Ges.* **44**, (5), 224–231 (1967).

[187] "Metallurgische Thermochemie," VEB Verlag Technik, Berlin, 1959.

[188] *Vak. Tech.* **10**, (5), 141–145 (1961).

[189] *Bull. Amer. Ceram. Soc.* **47**, (8), 493–497 (1968).

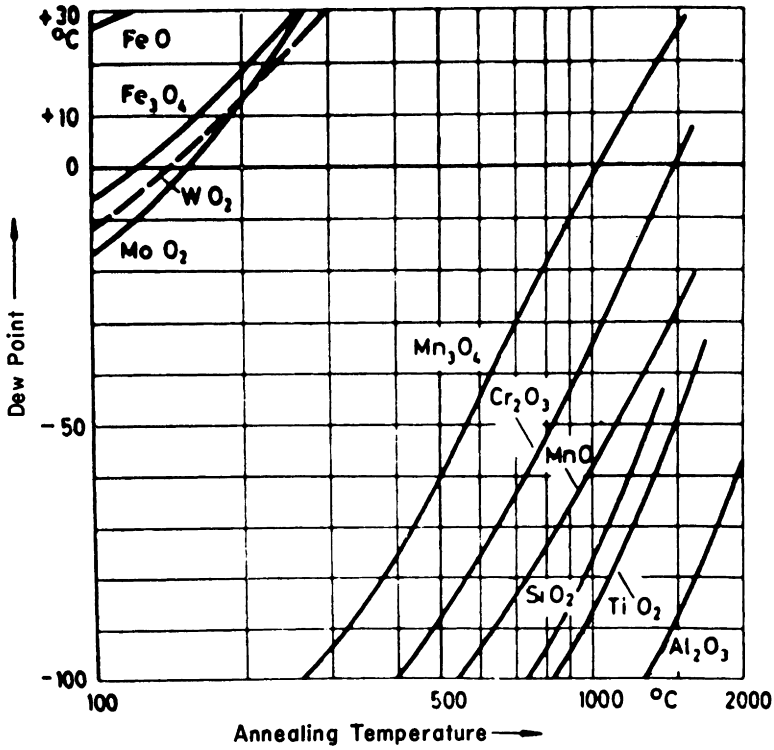


FIG. 129. Equilibrium curves for the systems of metal oxides in moist hydrogen as determined by Kotowski and Muschaweck. (Rochow.)

strains and stresses. A mix of 50 parts MnO, 30 parts SiO_2, and 20 parts Al_2O_3, plus 30 volume % Mo powder can be used for alumina-ceramics, fired at 1400°C to achieve a firmly adherent coating that corresponds approximately to optimum conditions for the thermal expansion properties of the components of such "metallized" composites. Even single crystals of sapphire can be metallized in this manner. In the microtexture of such metallized sealings, the characteristic crystalline new formation of galaxite, $MnAl_2O_4$, was identified.

610. More recently, J. T. Klomp and Th. P. J. Botden[190] reported on direct sealings of pure alumina-ceramics with iron alloys, prepared at 1140°C and higher, with $MnO-Al_2O_3-SiO_2$ melts or for special hard sealings on refractory metals at

[190] *Bull. Amer. Ceram. Soc.* **49**, (2), 204–211 (1970); see also J. T. Klomp, *Ber. Deut. Keram. Ges.* **47**, (10), 627–629 (1970).

1300°C and higher, with melts of the system $CaO-MgO-Al_2O_3-SiO_2$. In principle, such hard sealings and common glass/metal sealings differ much in thermal-mechanical properties. The application of the Mo sealing method is demonstrated for diversified crack-free production operation over a wide range of compositions and fusion temperatures increasing stepwise (from 1140° to 1500°C). In this case, calcium aluminate mixtures ($12CaO \cdot 7Al_2O_3$ and others) are sealed at 1500°C making possible the solution of difficult problems of a fully high-vacuum-tight finish for special rotation shapes. Many details of most recent experience in this fascinating field are found in another article by J. T. Klomp[191] from which we selected a characteristic diagram of electron-beam microprobe analytical results for the Mo–Al distribution in depths of 0–30 μ from the surface of the sealing (Fig. 130).

611. Lead borates and lead Cabals, as discussed in Vol. VII. ¶ 40 and 692 after A. Abou-El Azam and H. A. El-Batal,[192] have low softening (Littleton) point tem-

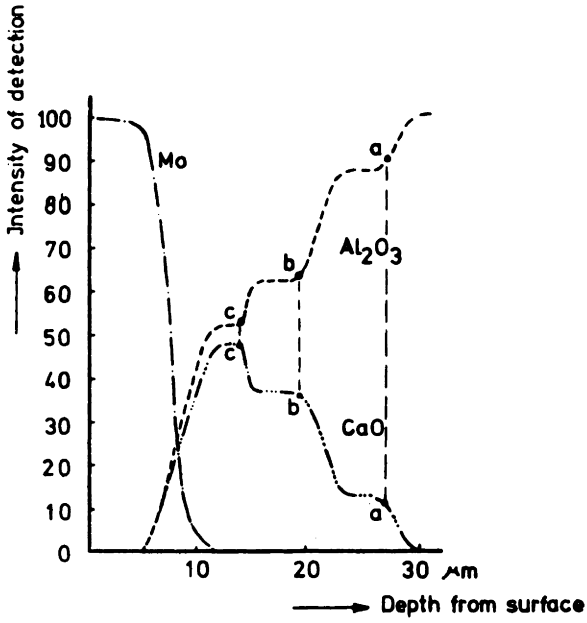


FIG. 130. Intensity curves of Al_2O_3; CaO and Mo, of the pure dense alumina/metal interface, measured with the Norelco electron probe microanalyzer. (Klomp.) Points *a* correspond to the real Al_2O_3 and CaO concentration in $CaO \cdot 6Al_2O_3$; points *b* correspond to the real Al_2O_3 and CaO concentration in $CaO \cdot Al_2O_3$; points *c* correspond to the real Al_2O_3 and CaO concentration in $12CaO \cdot 7Al_2O_3$.

[191] *Powder Metall.* **3**, (3), 142–146 (1971).

[192] *Phys. Chem. Glasses* **10**, (4), 159–163 (1969).

peratures; they find a certain interest for metal sealings for special purposes. A. F. Abbas and H. A. El-Batal[193] described glasses containing Co that have a magnetic mass susceptibility in counteraction with the diamagnetic characteristics of the parent glass, as measured by the Mettler magnetic balance.

612. Problems in the development of acid corrosion resisting *cast iron enamels* were studied by O. Gerstmann and A. Petzold.[194] The metallographic texture of cast iron with its inherent heterogeneities causes differences in the properties of near-surface and inner portions and the ensuing progressively increasing surface oxidation defects. Gerstmann and Petzold systematically varied the firing conditions of the ground enamels as they are conventionally applied onto cast iron, and transferred them to those of the cover enamel at 900°C to develop a ferritic structure in the surface layers which were later sand blasted. The kinetics of the oxidation reactions correspond to the Tammann law $x^2 = kt$ (x, the mass increase; t, time), first with a wüstite layer developed, then with hematite as the oxidation product of FeO. Nevertheless, the rate of oxidation is different for thinner and thicker layers with considerable scatterings over the temperature range from 800° to 900°C, as a consequence of the heterogeneous structure of Fe – C alloys causing anomalies in the thermal expansion, and even cracking along the graphite-filled veins. Overlong oxidizing firing causes "overburning" of the enamel which gradually loosens from the metal surface. Further overburning finally causes crystallization of magnetite. An optimum adhesion strength and absence of surface pores is achieved mostly by firing for only 2 minutes at 850°C, for application of the cover enamel to the ground enamel.

613. In the manufacture of *wire glass* (steel wires in glass fibers) K. Nagano[195] observed a spontaneous evolution of gas bubbles (blisters) originating as a constant rule from cracks and local structural constituents like cementite and pearlite exposed by the fracture, which are a product of reactions between the iron surface and the (regularly added) lubricant materials. The best way to avoid these anomalies and defects is to choose a steel as low in carbon content as possible or to chose "decarburized" steel sheets. Also no bubble formation takes place when the temperatures of the wire drawing are below 300°C.

614. The nature of the gases evolved during enameling, and their effects on iron case enameling were studied by V. G. Upadhyaya, H. O. Mulfinger, and A. Dietzel,[196] who emphasized the integral role of the water vapor content of the furnace

[193] *Bull. Centr. Glass Ceram. Res. Inst. (Calcutta)* **17**, (3), 76–82 (1970).

[194] *Silikattechnik* **15**, (4), 123–128 (1964).

[195] *Asahi Garasu Kenkyu Hakoku* **18**, (1), 1–10 (1968).

[196] *Bull. Centr. Glass Ceram. Res. Inst. (Calcutta)* **14**, (2), 35–59 (1967), with valuable literature references.

atmosphere, in the correct or anomalous course of enameling reactions (see ¶ 387). To avoid repeating our earlier comprehension of the important results and conclusions of those investigators (¶ 596), we mention only that experience shows many times the occurrence of oxidized cast iron and blistering in the enameling process; that blister-free enameling is possible when the cast iron is fired in an oxygen-free surrounding atmosphere. Gases that provide suitable atmospheres to overcome blistering are hydrogen, CO, CO_2, and water vapor.

615. Conventional *testing methods* for the mechanical quality of steel sheet enameling products like the well-known impact or torsion tests, are as a matter of principle, in no way less significant than the *bending test* for enameled steel strips, bent over an arc (see Fig. 131) or the improved Danielson–Lindemann test.[197] K. H. Clemens[198] reports that certain shortcomings of the latter-mentioned method can be avoided by applying the principle of a logarithmic spiral shape for the arc length measure shown in the principle sketch (Fig. 132) for the back support of the strip sample to be chucked. The mathematical evaluation for this modification and its numerical evaluation for the properties of the enameled steel material can be applied with a satisfactory accuracy and reproducibility demonstrated for a series of very different enamel types of conventional and special composition. The rupture radius accurately measured can then be used for the no less satisfactory calculation of the steel elongation, and the strain at the moment of rupture.

616. Particularly important and instructive comparisons are made by A. E.

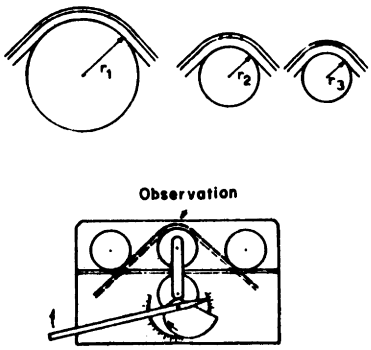


FIG. 131. Principle of bending test device according to Danielson and Lindemann, over cylindrical mandrels. (Clemens.)

[197] Cf. A. I. Andrews, "Porcelain Enamels, Preparation, Applications, and Properties of Enamels," 2nd ed., p. 567, Garrard Press, Champaign, Ill., 1961.

[198] *Mitt. Ver. Deut. Emailfachleute* **18**, (1), 1–6 (1970).

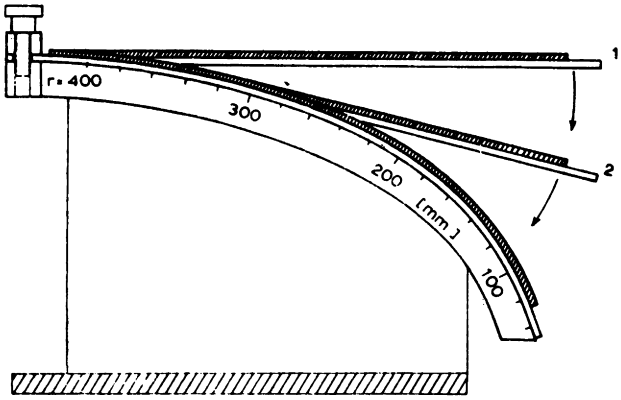


FIG. 132. Bending test over a mandrel in the shape of a logarithmic spiral. (Clemens.)

Nowak, R. Brückner, and H. W. Hennicke[199] for testing successive surface abrasion effects by the rapid centrifugation impact of sand on an enameled sheet sample. For the accurate observation and evaluation of experiments of this kind, it is essential to use different methods—by measuring changes in light reflectance of the sheets and the light-scattering effects ensuing by determination of gravimetric data in the weight losses during the progress of abrasion, or by testing with a surface caliper. These methods supplement one another in conclusiveness; the second method indicates the advanced state, the first and third the initial wear conditions in a linear functional correlation between the measured results, and the effective surface abrasion with the optimum of sensitivity. The slope of the linear functions may be used as a measure of the wear resistance or the susceptibility to corrosion.[200]

617. For chemical corrosion tests of enamels, A. E. Nowak, R. Brückner, and H. W. Hennicke,[201] in addition, described the efficiency of an *optical* device, and a method based on the principles of light reflection and scattering, the gravimetric determination of mass losses, and the mechanical caliper (feeler) methods. The results of chemical corrosion after exposure of enamel surfaces to etching in 1/10 *N* solutions of HCl or NaOH, show highly variable characteristics in a series of conventional and newly developed enamels, be it by prevailing cation-exchange mechanisms, or in numerical dissolution data from chemical reaction on the sur-

[199] *Mitt. Ver. Deut. Emailfachleute* **18**, (5), 19–26 (1970).

[200] The sand centrifugation device was described by A. Dietzel and M. Buck, *Mitt. Ver. Deut. Emailfacheute* **13**, (2), 9–14 (1965); characteristic examples are given for the scattering indicatrix curves for the different apparatus applied, and surface profiles as determined by the Leitz–Forster caliper tester,

[201] *Mitt. Ver. Deut. Emalflachleute* **18**, (8), 30–35 (1970).

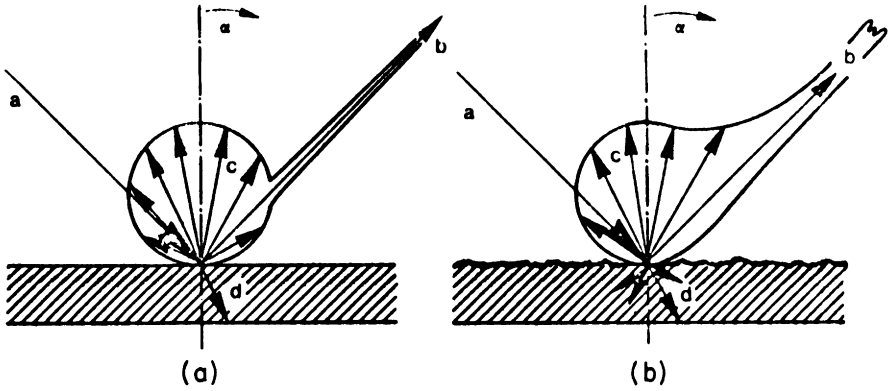


FIG. 133. Scattering indicatrix with reflexion peak; (a) for a smooth surface, (b) for a rough surface. (Nowak, Brückner, and Hennicke.)

faces. For these extensive experiments, the scattering indicatrix curves (Fig. 133) and profile tester curves are demonstrated.

CONSTITUTION AND PROPERTIES OF CERAMIC GLAZES

618. We may introduce this technologically important Chapter by a brief characterization of the meritful investigations made by A. S. Watts which extended over a decade and are introduced by four illuminating publications under the collective title "Control of the Properties of Glazes with the Aid of Eutectics." These are studies of the fusion behavior and other fundamental properties of mixtures, the composition of which is represented by "eutectic areas" in polynary phase diagrams, as the basic idea to be systematically pursued throughout the series. The first of these considerations concerns the most important silicate and aluminosilicate systems for preparing useful ceramic glazes.[202] The purpose of these first orienting studies was the detection from system to system of those compositions which are characterized by the "lowest deformation" degree as an indicator of eutectic complexes, and the temperatures of sudden ("abrupt") fusion ("liquefaction"). As an example of the graphic treatment in Watts' plotting methods, the system $SrO-Al_2O_3-SiO_2$ as shown in the diagram Fig. 134, may make evident the coincidence of the "deformation eutectic" with the composition having the most "abrupt" deformation.

[202] *J. Amer. Ceram. Soc.* **38**, (10), 343–352 (1955), namely the aluminosilicate complexes of the type $RO-Al_2O_3-SiO_2$, with R = Ca, Mg, Sr, Ba, but also Zn and Pb. The phase diagrams are taken from the classical results of investigations by the staff of the Geophysical Laboratory (Carnegie Foundation of Washington, D.C.) from 1910 to about 1940 (cf. III.B. of the series "Silicate Science," 1965).

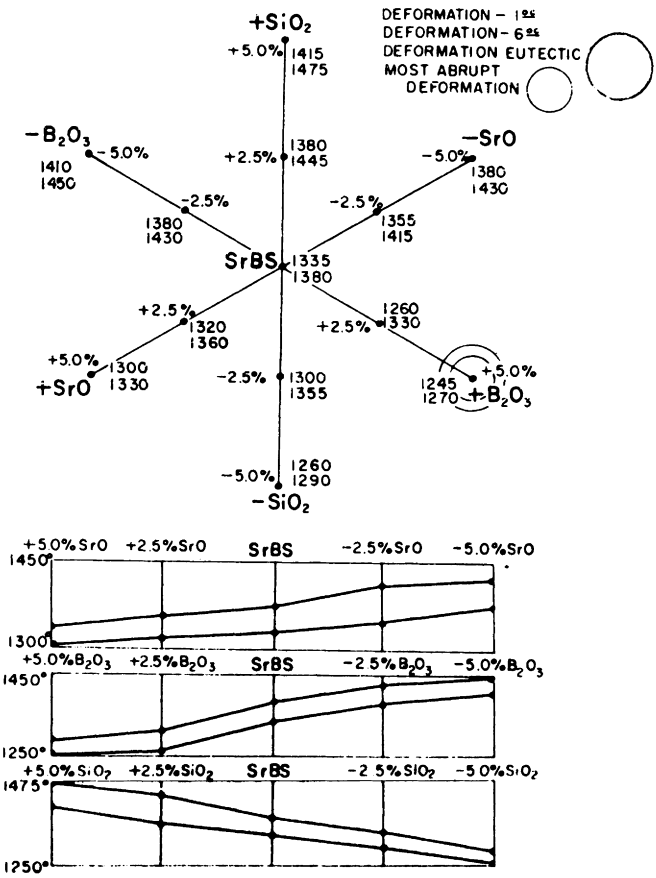


FIG. 134. Deformation data for $SrO-B_2O_3-SiO_2$ glasses near the composition of 34.1% SrO, 32.7% B_2O_3, 33.2% SiO_2. All glasses in this area are insoluble. (Watts.)

619. A second publication[203] includes analogous considerations of the alkali aluminosilicate systems, $R_2O-Al_2O_3-SiO_2$, (with R = Li, Na, K), and the important system $PbO-Al_2O_3-SiO_2$, in binary and ternary combinations from the same viewpoints of essential glaze-forming properties as it was done in the first publication, but now extending to the solubility behavior of such complexes in dilute acids and alkaline, or phosphate solutions, with regard to the practical usefulness of glazes. The lowest deformation temperatures, and the rates of fusion as experimentally measured, were also recorded in the "eutectic areas" (see above), from system to system. A separate evaluation of alkali-lead aluminosilicate systems

[203] *J. Amer. Ceram. Soc.* **41**, (7), 249–253 (1958).

in their eutectic complexes and glazelike melt properties were plotted in a corresponding manner. In this type (α) of aluminosilicate complexes one may also count glasses of the system $MgAl_2O_4-LiAlSi_2O_6$, which were studied by N. A. Toropov, N. A. Sirazhiddinov, and N. Rakhmanbekov.[204]

620. In addition, Watts studied under the same leading ideas the systems of alkaline earth oxides with *boric acid* and silica to select from available frit mixtures expected to be a minimum solubility character.[205] Again, the individual solubility data in acidic, alkaline, and phosphatic solutions were chosen as an important criterion for selection of borosilicate compositions as convenient B_2O_3 sources for ceramic glazes; that best "insoluble" complex composition which was highest in B_2O_3 in each individual system was chosen for a "triaxial" diagram of sources of possible glaze batches, i.e., of borosilicate frits for the ensuing combination with ceramic bodies in manufacturing practice. Again, the most "insoluble" compositions were studied in detail for the effect of limited changes in composition in respect to their softening (deformation) temperature and the rate of deformation. The alkali$-B_2O_3-SiO_2$ systems[206] are the last illustration in Watts' systematics, extended also to polynary compositions K_2O, $Na_2O-PbO-B_2O_3-SiO_2$ to serve as "sources" for the introduction of B_2O_3.

621. Glazes of a composition in the system $Na_2O-CaO-B_2O_3-Al_2O_3-PbO-SiO_2$ were extensively examined by G. J. and W. Roberts, S. Salt, and C. E. L. Franklin[207] for density, refractive index, Youngs' modulus, thermal expansion coefficient, gloss value, microhardness, flow length (principle of the channel Button test), and viscosity (cf. ¶ 578, 582). All these data are of great significance in the practical application of such glazes, and to indicate the specific influence exerted by changes in the content in alumina, B_2O_3, and CaO on the flow characteristics.

622. Concerning the *raw materials for glaze* manufacturing, a report presented by P. Mandt[208] discusses the application of the ternary system of feldspar with petalite and wollastonite, i.e., as a partial system of the polynary $Li_2O-K_2O-Na_2O-CaO-Al_2O_3-SiO_2$ complexes. Here, the favorable effects of Li aluminosilicates like petalite, $Li_2O \cdot Al_2O_3 \cdot 8SiO_2$, are remarkable for their improvement of the translucency of ceramic bodies prepared with such complex batches, and for the negative contribution of this addition to expansion, which facilitates an adjustment of glaze fit on the ceramic substratum. A detailed discussion of the

[204] *Uzb. Khim. Zh.* **11**, (2), 7–19 (1967), (cf. III.B. ¶ 221 ff.).
[205] **44**, (6), 272–276 (1961).
[206] Cf. **46**, (8), 371–373 (1963).
[207] *Trans. Brit. Ceram. Soc.* **63**, (10), 553–562 (1964).
[208] *Ber. Deut. Keram. Ges.* **42**, (10), 385–391 (1965).

important cone fusion tests shows impressively the "eutectic fusion" phenomenon for the mixtures of the three minerals.[209] The ternary minimum corresponds to a body relatively high in petalite, low in feldspar, and moderate in wollastonite content, with an extremely low end point for the pyrometric cone examination (Seger cone No. 8). The ternary mixtures are useful for glazing soft and hard porcelains equally, but have a certain tendency to be overfired. For this reason, the use of petalite should not be above a certain practice-determined critical limit.

623. Commercial *salt glazes* containing B_2O_3, ZnO, and MnO show, in microscopic studies made by E. R. Segnit,[210] a crystallization of willemite, Zn_2SiO_4, and a yellow spinel (chiefly gahnite) and may contribute to the peculiar bronze luster of such Mn-containing glazes which substitutes Fe in silicates and oxide phases. Interesting is the possible crystallization of a new compound $2Na_2O \cdot 2ZnO \cdot 3SiO_2$.[211] Practically, it is remarkable that it is not necessarily beneficial to add NaCl or borax to the batch of an efficient "salt glaze", e.g., for red-firing heavy clay ware.[212]

624. The flow behavior of glazes in the fritted state as a general criterion of quality and degree of suitability for ceramic glazing purposes, was studied by K. Beyersdorfer and J. Hammer[213] by improving the manipulation and reproducibility of mechanical improvements, e.g., by application of a very thin preglaze onto the surface of the flow channel in the test plate (inclination angle to the horizontal orientation = 45°) with the same glaze that is to be tested. The device recommended automatically measures the softening temperature of the glaze sample under a load when the test pellet is heated with a constant rate. A plunger shaped of pure alumina ceramics (Degussite brand) tapering to 0.5 mm^2 at the pointer exerts a load of 40 kg/cm^2 onto the top of the pellet; when this plunger has penetrated to an accurately defined distance, the temperature is automatically recorded. It then corresponds to a viscosity of the test material $\log \eta = 10$. Opaque, or early devitrifying glazes do not, in general, give well reproducible results with this flow test device, but the softening temperature of the material is commonly so far below its crystallization temperature that the method can be used, nevertheless, as an indicator of a step which is important enough to characterize the quality of the given glaze, even when the glaze already contains crystalline particles suspended. The method follows the general principles of the channel flow tests which are standardized for many specifications,

[209] Cf. H. Salmang, "Die Keramik," 4th ed., pp. 182 ff. Springer Verlag, Berlin, 1958.

[210] *J. Aust. Ceram. Soc.* **2**, (2), 32–37 (1966).

[211] Cf. E. R. Segnit and A. E. Holland, *Aust. J. Chem.* **19**, 905–913 (1966).

[212] Cf. D. R. Foster, Bull. No. **113**, Ohio State Univ. Studies, Eng. Series, 1942.

[213] *Ber. Deut. Keram. Ges.* **43**, (10), 567–571 (1966).

e.g., the DIN 51 064 prescription for measuring the softening temperatures under a controlled pressure.

625. That *thermographic* methods (e.g., the differential-thermal analysis, and the like) for the control and production of glazes and frits are of special value for an improved technological examination during those processes is demonstrated in an article by O. K. Kukur, A. Ya. Vaĭvad, and Yu. Ya. Eĭduk,[214] specifically to survey complete dissolution of sand grains and other residues from batches in the glaze melts, beginning crystallization, unmixing reactions, and gas evolution. This application of the differential-thermal analysis is shown for a series of frits containing, besides the normal oxidic constituents, *fluorides*, PbO, B_2O_3, and iron oxides, building-up ternary, quaternary, and polynary oxide complexes. The constitution of these is approximately known from the phase equilibrium diagrams of the systems. The interpretation of numerous types of thermographic curves for complexes and products concerns chiefly a discrimination of the exothermic and endothermic effects (peaks) of softening and melting phenomena in the frits and finished glazes.

626. Difficulties arising in the production of a half-crystalline coating by common enameling techniques are seen by M. L. Zorina, E. M. Milyukov, and D. F. Ushakov[215] in trying to find a composition which would not restrict the controlled volume crystallization. Without some primary crystallization, it is not possible to reach total uniform crystallization in the temperature range of 550° to 560°C. Uniform crystallization may be achieved, however, by a 4-hour period of pre-crystallization at, say 500° to 550°C. The mechanical and thermal properties of the products are not affected by these manipulations; the crystallization products in question are TiO_2, α-$LiAlSi_2O_6$, and α-$LiAlSiO_4$, (cf. Vol. III.B ¶ 145 ff.).

627. In *scavenging* high-level radioactive *nuclear wastes* in glass and other ceramic materials, problems may arise from the solubility of Ru^{106} among the fission products. This element is relatively easily volatilized as RuO_3 (above 1300°C), whereas ruthenates with the anion $(RuO_4)^{2-}$ are only sparingly soluble in glass, as J. Mukerji and S. R. Biswas observed.[216]. The solubility of Ru in Na silicate glasses with 20 to 33 mole % Na_2O over the temperature range from 1000 to 1400°C rapidly increases for the ratios above Na_2O/SiO_2 = 1:3 and above 1200°C, with a steeper slope on the solubility versus temperature curves. Evaporation of Ru is likely to be acute

[214] In the book "Vitreous Systems and Materials" (Yu. Ya. Eĭduk), pp. 59–66, Izd. Zinatne, Riga, 1967.

[215] *Izv. Akad. Nauk SSSR Neorgan. Mater.* **3**, (3), 503–508 (1967).

[216] *Bull. Centr. Glass Ceram. Res. Inst.* (*Calcutta*) **14**, (2), 30–34 (1967); see also *Trans. Ind. Chem. Ceram. Soc.* **28**, 59–62 (1969), on the spectroscopic determination of complex compounds of Ru in KOH solutions; this element can occur in the tri-, tetra-, or six-valency state in Na silicate glasses.

at temperatures above 1200°C, and for glasses with Na_2O/SiO_2 above 1:3. In every case, the volatilization of Ru from a glass surface takes place on the way over a solution phase of RuO_2 in glass. For scavenging radioactive Ru from nuclear wastes in Na silicate, and Na phosphate glasses, Biswas and Mukerji[217] investigated the solubility of this element also in borophosphate and lead phosphate glasses. The solubility is higher in the borophosphate glass; an addition of B_2O_3 to Na phosphate glass slightly increases the solubility of Ru until a maximum is reached at about 5 mole % B_2O_3, irrespective of the composition of the base glass. The lead phosphate glasses investigated showed a very striking maximum for the Ru solubility at 45 wt. % PbO.[218]

628. The *optical properties* of ceramic glazes were intensively investigated by K. Doerbecker and H. J. Oel[219] using an X-ray diffraction goniometer, somewhat rebuilt (modified to adapt optical measuring methods) for the glaze surface as a function of the angle of reflection, and a variable angle of incidence. In this way, it was made evident that it is possible to measure accurately every change of the glaze surface caused either by abrasion or corrosion. Corrosion can be observed in very early stages. Common glazes always show a superposition of mirroring, turbidity and "frosting" phenomena, except that frosting is not observed on fresh (virginal) surfaces. In this way, the curves are composed of the cosine function for the turbidity, and a superimposed pointer for mirroring effects (typical examples are demonstrated by Figs. 135–137), the cosine curve being higher or lower, corresponding to different degrees of remission; the curves vary characteristically with increasing "frosting," the longer the glass surface was sprayed with SiC powder. The reflection data react highly sensitively to changes in the rugosity of the surface; the slope of the scattering indicatrix is also much more sensitive than is the mere visual impression, and offers more abundant information on the properties of the samples under test than any other qualitative estimation.

629. Examination in *polarized* light, as discussed in the second publication by Doerbecker and Oel, means a considerable increase in accuracy for the indicatrix measurements, and improvements in the discrimination power among the three fundamental effects of mirroring, turbidity, and frosting. This has great signi-

[217] *Bull. Centr. Glass Ceram. Res. Inst.* (*Calcutta*) **15**, (4), 99–103 (1968).

[218] Concerning the application of glasses for scavenging the Ru^{106} for the storage of nuclear wastes, cf. W. E. Clark and W. H. Godbee, on "Fixation of Simulated Highly Radioactive Wastes in Glassy Solids"; and M. N. Elliot, J. R. Grover, and W. D. Hardwick, on "Experimental Fixation of Radioactive Wastes in Glass. Experimental Evaluation of Phosphate and Borosilicate Glasses," pp. 411–439, Internatl. Atomic Energy Agency, Vienna, 1963.

[219] *Ber. Deut. Keram. Ges.* **45**, (3), 116–121 (1968); **45**, (9), 478–482 (1968).

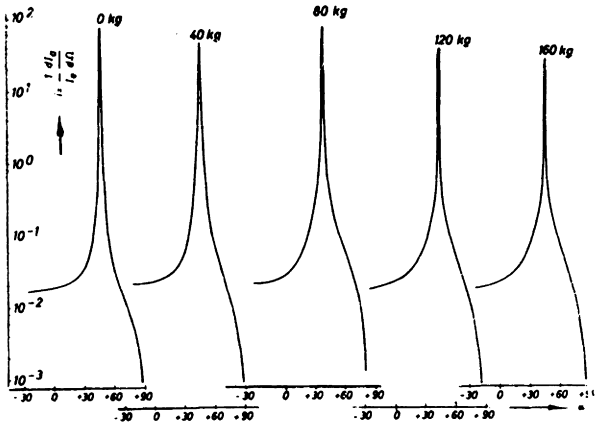


FIG. 135. Typical scattering indicatrix diagrams of different ceramic glaze surfaces. (Doerbecker and Oel.) A hard porcelain with brown glaze, the nontreated sample showed frosting.

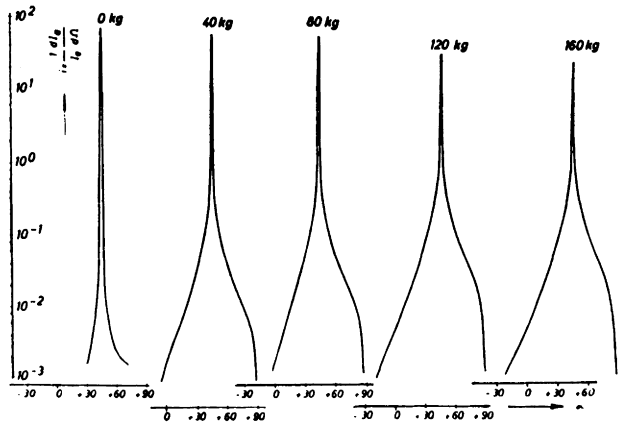


FIG. 136. Window glass; light reflection starts from the front and back side of the glass plate equally. (Doerbecker and Oel.)

ficance for the study of corrosion effects by simple surface abrasion and chemical corrosion. The frosting effects seen in polarized light are well characterized as the cooperation of onefold or of double reflection by elementary "micromirrors" (reflecting particles), in different orientations. From this model concept, a comprehensive theory of the frosting effects could be developed. In this way, frosting can be related to the better defined variables of surface rugosity. *Depolarization* effects can occur only when the light beam is deflected at least once from the plane

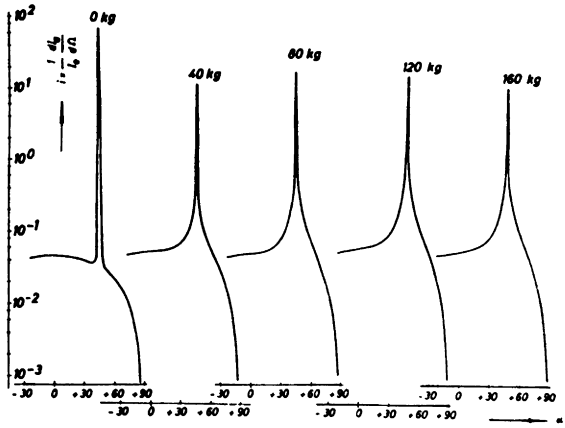


FIG. 137. Wall tile with black glaze; compare the intensity of cosine with that of brighter glazes. (Doerbecker and Oel.)

in which the incident light ray and the normal perpendicular to the sample surface are defined. An example of the practical evaluation of the scattering indicatrix as determined in polarized light is given in Fig. 138, for a hard porcelain coated with a brown colored glaze, after different degrees of frosting by sprinkling with a fine powder of silicon carbide over fritting glazes for all kinds of decorating in ceramic arts. Many technological details are presented for the correct use of coatings.

630. W. Wanie[220] reviewed a wealth of information material on *colored* ceramic bodies, engobes (equal to coating slips), and their fitting glazes for diversified kinds of ceramic decorating, and technological details of coatings, e.g., for roof tiles, face bricks, common household pottery, stove tiles, and the like. Of great value is the chemical-technological instruction in color reactions from the raw bodies before and after firing changes of colors in coatings as a function of the partial pressure of oxygen in the kiln atmosphere, and related practical problems, interreactions between ceramic substrata and the coating for adhesion and color tints. Special instructions concern the handling of difficult and critical color effects (e.g., with Se-red glazes) or for achieving a high whiteness (with SnO_2 as the source; on TiO_2 whitening, cf. ¶ 635 ff., 650).[221]

[220] *Glass Email Keramo Tech.* **19**, (6), 198–206 (1968); **19**, (7), 236–242 (1968).

[221] Concerning practical problems of chemical durability for the industry and related problems, we refer to ¶ 583, 612, 617, 619, and the publications by A. Dietzel *et al.*, e.g., A. Dietzel and H. J. Oel, *Mitt. Ver. Deut. Emailflachleute* **16**, (11), 81–85 (1968).

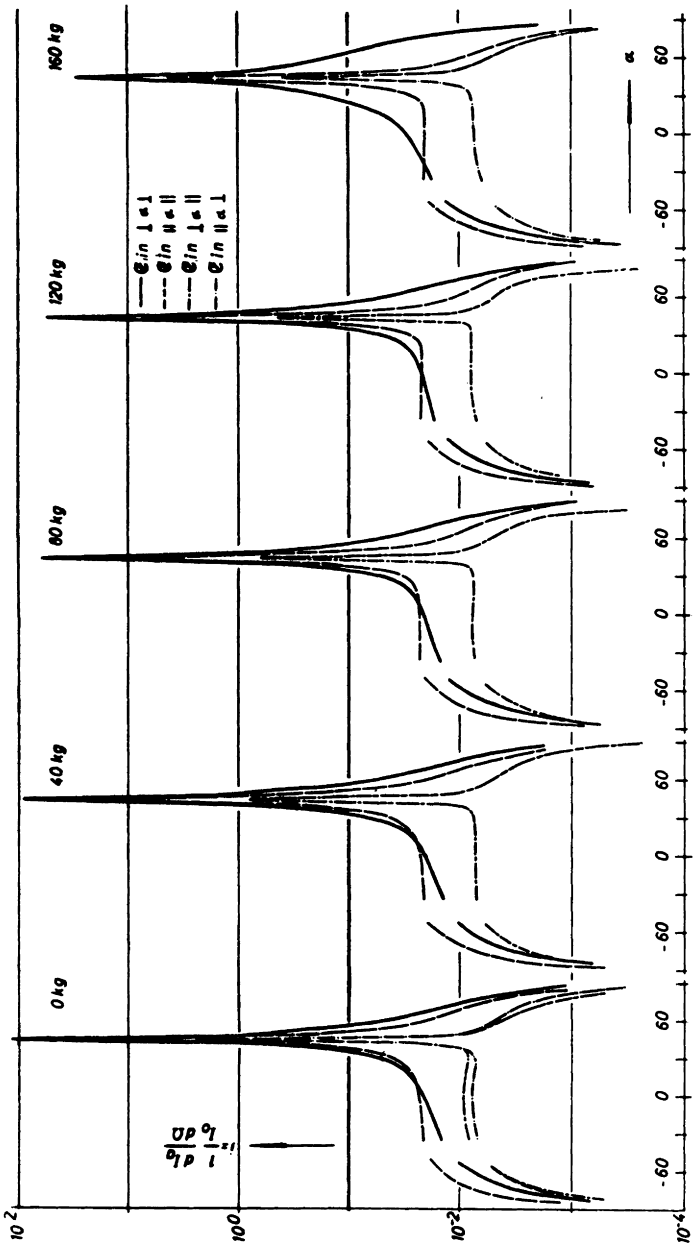


FIG. 138. Scattering for a hard-porcelain with brown glaze (Fig. 135), after a surface spraying with fine-ground silicon carbide and testing in polarized light (Doerbecker and Oel.)

631. We do not wish to omit from this chapter a brief characterization of advancements in the interpretation and elimination of the well-known defects of glazes by *crawling* (often called "balling-up") as discussed by D. W. Budworth.[222] This author showed that for a layer of non spreading liquid (finite contact angle $\Theta = 0$) on a ceramic or metal substratum, there is a critical thickness: $t_c = [2\gamma_{LV}(1 - \cos\Theta)/\rho g]^{\frac{1}{2}}$ γ_{LV} being the surface energy on the contact of liquid/vapor phase, ρ the density of the liquid, g the gravity acceleration constant). Glazes often have thicknesses below t_c; therefore, they have a *natural tendency* to crawl. An unbroken glaze layer is in a remarkably metastable equilibrium state relative to the crawled state.

NUCLEATED CRYSTALLINE OPACIFIERS IN ENAMELS AND GLAZES

632. C. G. Bergeron and C. K. Russell[223] observed the nucleation and crystal growth of lead titanate, $PbTiO_3$, as a highly efficient opacifier material, in a glass of composition 48.5 mole % PbO; 36.5 mole % B_2O_3; 15 mole % TiO_2, as a function of temperature. On the theory of this reaction we refer to Sh. D. Brown and Ginell[224], with a very good agreement between the experimental results and the growth equation as developed by those authors, and its constants for a calculated activation energy of growth of 34 kcal/mole (in comparison with the activation energy of viscous flow at 750°C of 75 kcal/mole). Of general importance is the observation that the differential-thermal analysis curves (cf. Fig. 139) of the glass powder show peaks for exothermic reactions at temperatures which are 100° to 150°C lower than the temperature of maximum crystal growth (750°C). This apparent anomaly is interpreted as a shifting of the rate of nucleation in the higher specific surface of the glass powder material.[225]

633. In the observation of high-dispersed crystalline opacifier materials in glasses, enamels, and glazes, the detection of their substance is greatly facilitated by X-ray low-angle scattering methods. C. K. Russell and C. G. Bergeron[226] used such methods in studies on the crystallization in the system $PbO-Al_2O_3-TiO_2-SiO_2$.

[222] *Trans. Brit. Ceram. Soc.* **70**, (2), 57–59 (1971).

[223] *J. Amer. Ceram. Soc.* **48**, (3), 115–118 (1965).

[224] "Symp. on Nucleation and Crystallization in Glasses and Melts", pp. 109–118, *Amer. Ceram. Soc.*, Columbus, Ohio, 1962, (cf. VII. ¶ 331).

[225] Cf. the same authors, and A. E. Friedberg, *J. Amer. Ceram. Soc.* **46**, (5), 248 f. (1963). (cf. ¶ 346, 574), see also Vol. III.A., ¶ 29, footnote 31.

[226] *J. Amer. Ceram. Soc.* **44**, (5), 268–271 (1965); (cf. VI.C. ¶ 175; VII. ¶ 352, 548, to which we refer for details).

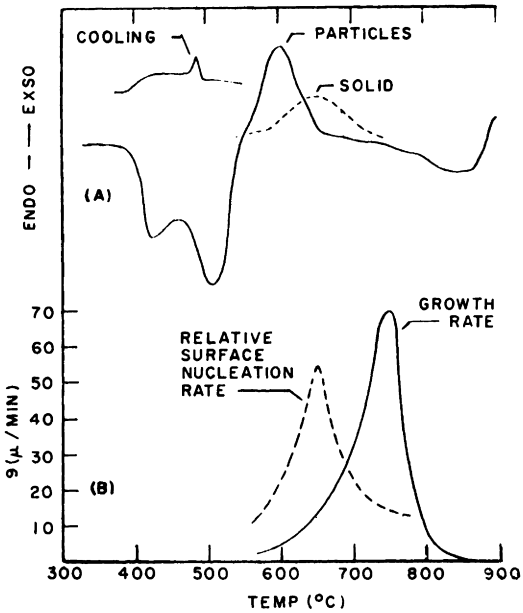


FIG 139. (A) Differential-thermal analysis curve of glass; (B) growth rate, and relative nucleation rate of $PbTiO_3$ from glass, as a function of temperature. (Bergeron and Russell.)

634. We may remark that the lead titanates mentioned above according to the observations made by Bergeron and Russell, may (after F. W. Martin[227]) appear in lead borosilicate glasses containing 10 to 20% TiO_2 not only in the well-known pseudocubic (tetragonal) *perowskite* type, but also in a *cubic* phase which is metastable. It was observed thus from a glass with 72 wt % PbO, 15–20 wt % TiO_2, 8 wt % SiO_2, 4 wt % B_2O_3 as a vividly yellow-colored crystalline phase which is precipitated above 570°C and inverted to the stable tetragonal product. At lower temperatures this metastable titanate has the structure of pyrochlore which is cubic with space group $O_7^h = F\,d3m$ and the parameter $a_0 = 10.4$ Å. The general composition type corresponds to the formula $A_2B_2O_7$ and mostly contains some silica, in addition. By leaching in appropriately dilute HNO_3 acid, the pyrochlore-type crystal phase can be isolated and studied in every detail in its conversion behavior to perowskite type $PbTiO_3$ at elevated temperatures. The conversion temperature is well defined on the curves of differential-thermal analysis in an exothermic reaction peak near 570°C. Highly remarkable is the structural analogy of $Pb_2Ti_2O_7$ with $Cd_2Nb_2O_7$, one of the

[227] *Phys. Chem. Glasses* **6**, (4), 143–146 (1965).

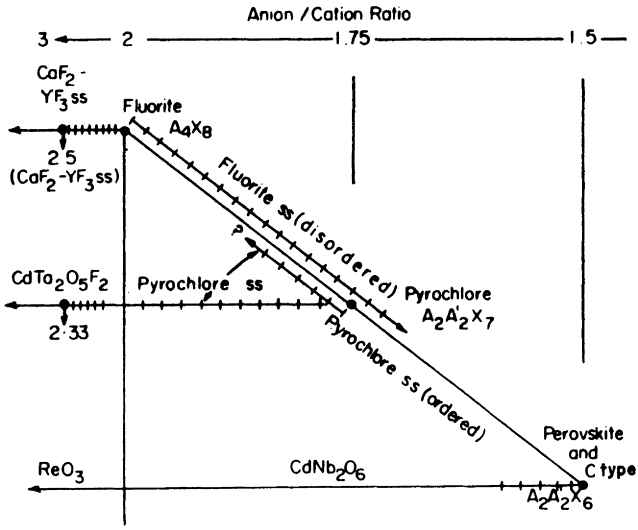


FIG. 140. The chart is to show compositional and structural correlations between pyrochlore and other crystal types like fluorite and perovskite. Crystalline solubility relations are indicated by the hatched lines. Two series exist of defect crystalline solutions between pyrochlore and fluorite, a high-temperature disordered series (of fluorite type) with anion vacancies, and a lower-temperature series (of pyrochlore type) anion vacancies-ordered series. (Aleshin and Roy.) Ratios A/X greater than the normal are realized in pyrochlore and perovskite by a cation-vacancy mechanism, in fluorite by an interstitial anion vacancy mechanism.

most interesting, newer semiconductor materials, with quite particular dielectric properties.[228]

635. The kinetics of the *anatase* ⇌ *rutile* inversion is a typical example for a monotropic reaction; in the observation of the sigmoidal inversion versus time curves the nucleation of the more stable crystalline phase is indicated, namely, primary anatase and the progressive growth of rutile in its place, as demonstrated by R. D. Shannon and J. A. Pask.[229] Starting from commercial anatase powders, the kinetic analysis of the inversion curves was attempted in the interpretation by following three stepwise reactions and corresponding equations as was proposed by W. F. Sullivan and S. E. Cole,[230] as a first order process. The activation energies, as calculated, varied

[228] Cf. J. Jona, G. Shirane, and P. Pepinski, *Phys. Rev.* **98**, 903–909 (1955); especially on the crystallochemical akinships in the structures of fluorite, pyrochlore, and perovskite, types see an instructive chart presented by E. Aleshin and R. Roy, *J. Amer. Ceram. Soc.* **45**, (1), 18–25 (1962); and Fig. 140.

[229] *J. Amer. Ceram. Soc.* **48**, (8), 391–398 (1965), with a highly valuable reference literature for further studies.

[230] *J. Amer. Ceram. Soc.* **42**, (3), 127–133 (1959), (cf. ¶ 572).

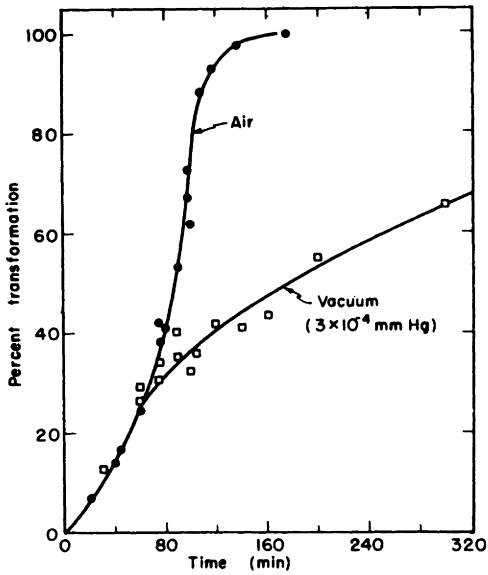


FIG. 141. Percentage of inversion of titanium dioxide (commercial sample) vs. time in air and *in vacuo* (3×10^{-4} mm Hg) at 1017°C. (Shannon and Pask.)

mostly in wide ranges, e.g., in the attempts made by those authors between 80 and 110 kcal/mole, evidently as a sensitive function of the presence of more or less minimal amounts of contaminations in the TiO_2 raw materials from which the samples had been prepared (Fig. 141). Shannon and Pask present a highly enlightening table of such impurity effects with controlled amounts of foreign oxides and ions as observed in the peak temperatures on differential-thermal analysis curves. However, no clear interpretations of the kinetic mechanisms could be derived from the different rate laws applied by different authors as full evidence of structural defects in the crystalline samples, mostly caused by the "thermal history" in the same manner as it is by contamination substances.

636. The presence of *copper*, which forms crystalline solutions with TiO_2 only up to 0.25 wt. %, in an atmosphere of hydrogen accelerated the inversion, whereas, a vacuum of 3×10^{-4} torrs inhibited the reaction. Acceleration may be combined with processes which increase the number of oxygen vacancy defects, whereas, retardation and even inhibition, may be caused by reagents which promote the content of Ti atoms on interstitial sites. Conclusions can be made, in every case, that deficiencies in oxygen vacancies caused by reduction with H_2 or the diffusion of Cu^{2+} ions form Magneli-type phases like Ti_nO_{2n-1}, to provide nucleation centers for rutile; *in*

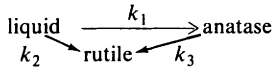
vacuo interstitial Ti^{4+} ions are formed by a structure "stuffing" effect which impedes the continuation of the inversion. A full general systematics could be evolved to explain the different reactivities of "contaminations" either by the presence of Cu^{2+}, Co^{2+}, or Li^{+} cations (with low electrostatic valence ions), and of other ions with higher valence numbers like P^{5+} or S^{6+}. A mere substitution of O^{2-} ions by F^{-} would reduce the number of anion vacancies, and therefore inhibit the inversion.

637. H. Rötger[231] used a titania-opacified fluorosilicate glass for studies of time-dependent opalescence and turbidity reactions, by experimentally varied exposures to aging and controlled "cooling" periods. The thermal-time program started from 950°C (i.e., above the liquidus temperature), with a cooling-down to 510°C (the aging temperature) with a rate of 50°C/hour. Special schedules of ensuing cooling and reheating then followed. The reappearance and disappearance of turbidity in different degrees were accurately measured. The transmissivity for light, the wavelengths of which were all in the range of the visual scale, was 50% (referred to a thickness of the glass layer) of 10 cm. At the start of the experimental series, the wavelength of 410 mμ was chosen but this was shifted during the aging to 714 mμ (over 24 hours). After reheating, however, the same optical effect required only 3 to 4 hours. The Rayleigh scattering parameter Q_{Ri^S} of the extinction modulus for the Lambert–Beer absorption law and changes in the refractive index and the density vary with the increasing segregation of turbidity centers (particles) to establish the time law of their condensation. Electron microscopy and X-ray diffraction analysis could be used for more-detailed studies of the nature of such particles; one day of thermal exposure, however, is not sufficient to make them visible in the electron microscope. Increasing degrees of crystallinity could be pursued in the curves after 16 days of exposure, to identify a dendritic growth previously described by W. Vogel.[232]

638. The long series of special publications by R. A. Eppler *et al.* concerns systematic investigations on the kinetics and physiography of titania-opacified cover coat enamels, and related ceramic products. We may first mention studies by R. A. Eppler and W. A. McLeran[233] which include quantitative X-ray diffraction measurements, specifically of the nucleation and crystal growth of TiO_2 (as anatase and rutile) in white enamels and glazes, as a function of time and temperature of maturing. As one important result of the evaluation of rich numerical and graphic diagram material three first-order processes, with the individual rate constants k_1, k_2, and k_3 (see the

[231] *Silikattechnik* **16**, (10) special issue, 423–427 (1963).
[232] *Silikattechnik* **10**, (5), 241–250 (1959).
[233] *J. Amer. Ceram. Soc.* **50**, (3), 152–156 (1967).

following sketch) must be distinguished;



i.e., one for the crystallization of anatase, another for that of rutile, and the third for the inversion of anatase into rutile, as a monotropic reaction. These evaluations established a model concept which fits a wide range of experimental temperature–time variables and curves. Anomalies, however, occurred when the thermal treatment ("firing") was too short or when it was done at too low temperatures. There are also pronounced misfits in the correlation between concentration and the crystalline phases, and finally only little correlation between reflectance and crystalline composition. To a certain degree, correlations with the Gardner color data were sufficiently helpful for practical aspects, although not perfectly reproducible.

639. *Spectrophotometric* measurements in pursuit of nucleation and crystallization in F-containing opal glasses were made by G. Paoletti and F. Giammanco.[234] The bell-shaped crystallization curves correspond to the light flux as defined in Rayleigh's theories as a function of concentration c, number, and dimension $D = 2r$, of spherical particles suspended in the glass matrix, in the simple expression $K = D^6c$.[235] For turbid glasses containing fluorides as the opacifying agents, the older theories of J. W. Ryde and R. D. Yates[236] might be applied which permit over the spectrophotometric data the derivation of crystal growth parameters. Interesting in the special glass type investigated by Paoletti and Giammanco is the crystallization of a *F-xonotlite*, $5CaO \cdot 6SiO_2 \cdot CaF_2$, at temperatures between 725° and 850°C; the maximum crystal size was observed over the temperature range from 780° to 800°C.

640. In optical glasses, the FICA (cf. S.O.F.I.C.A., 78 Le Misnil-St. Dénis, S. Lo., France; calibrated with benzene as a standard, or secondary standards, for wavelengths $\lambda = 436$, and 546 mμ) scatter photometer was used for analytical investigations by H. N. Daglish.[237] The FICA instrument permits a correction in the indications of *fluorescence* effects, and the elimination of a possible error which cannot be ignored since about two-thirds of commonly available glasses show a considerable fluorescence in the blue ($\lambda = 436$ mμ), whereas in green light ($\lambda = 546$ mμ) this share is negligible. Determinations of the *depolarization* ratio ρ at $\lambda =$

[234] *Verres Refract.* **23**, (6), 679–684 (1969), to be compared with observations by L. Prod'homme and C. Vacherand, *ibid.* **20**, (5), 354–361 (1966); cf. VII. ¶ 383.

[235] On Prod'homme's application of the Rayleigh–R. Gans approximation valid for coarser suspensions cf. *Rev. Opt. Theor. Instr.* **45**, (4), 167–176 (1966).

[236] *J. Glass Technol.* **10**, 274–294 (1926).

[237] *Glass Technol.* **11**, (2), 30–35 (1970), (cf. VI.C. ¶ 112).

900 mμ, could also be made with the FICA instrument as shown in a series of important optical and more common glass samples, including the near-infrared range. For relatively small scattering centers of slight anisotropy as a function of turbidity, $\tau = I - I_0 \exp(-\tau y)$ (y being the path length). These factors are of particular significance for the use of glass for fiber optics in wave guides, and optical transmittant systems in this wavelength range.

641. The purpose of a comprehensive theoretical and experimental study by R. A. Eppler[238] of *titania*-opacified white porcelain enamels for their crystallization behavior and phase inversion mechanisms (see above) was to develop equations describing the crystallization effects during the technological firing and maturing processes. It is basically important to know the rate of the anatase–rutile inversion measured in the percentage of the anatase crystallization, its solubility in the glass, and the rate of crystallization (see above). It is generally evident that treatment of the crystallization process as merely a reaction in the first order, is *not* admissible, as may be seen from Fig. 142, which shows in a semilogarithmic projection that there is no strictly linear correlation which would correspond to the conditions for a first-order

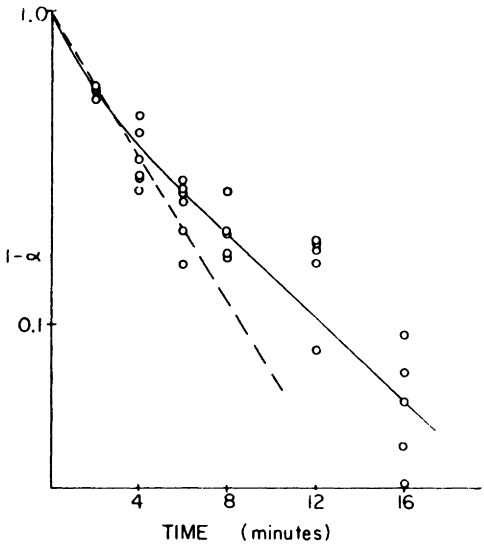


FIG. 142. Fraction crystallized from TiO_2–opacified porcelain enamel as function of time; quantitative X–ray diffraction data on samples fired at 700°C. *Solid line*, curve drawn through data means; *dashed line*, attempt to draw a straight line through data. (Eppler.)

[238] *J. Amer. Ceram. Soc.* **52**, (2), 89–94 (1969); **52**, (2), 95–99 (1969).

reaction; it is in contradiction to a best curvature approximation for the optical scattering data projection points. We cannot detail here the mathematical formulation and development of equations for the firing behavior of TiO_2-opacified enamels, so much the less because the Nernst treatment of the problem, which is usually attempted by starting from the diffusion theory, gives unsatisfactory approximative information. Somewhat better for this case is the Nielsen treatment which is based on the phenomenon of salt precipitation from solutions (e.g., for Ca oxalate, or $BaSO_4$).[239] The idea that *solubility* exposes a dynamic equilibrium between the rate at which the atoms arrive at the growing crystal and the rate by which they leave it again, is the decisive advancement in Nielsen's treatment of the problem.

642. The experimental studies of R. A. Eppler using the latter improvements to formulate final equations are based on quantitative X-ray diffraction measurements of titania-opacified enamels fired between 660° and 940°C. For a comparison, we present Figs. 143a,b, with data for anatase and rutile concentrations fired at different temperatures: 940° and 780°C for Fig. 143a, 800° and 740°C for Fig. 143b, respectively, as calculated from the X-ray measurements. The apparent activation energy for the inversion anatase → rutile is 87.4 kcal/mole, whereas the simplified theory (cf. Eppler and McLeran, see ¶ 638) gave 189 kcal; much better results were obtained by Shannon and Pask (see ¶ 635) with 108 to 148 kcal/mole, and by Sullivan and Cole (¶ 635) of about 100 kcal/mole. In every case, the anatase → rutile inversion is a strong function of temperature: the activation energy for the crystallization of anatase was calculated to be 32.0, that of rutile 28.3 kcal/mole.

643. In principle, the same fundamental ideas and facts are applied in R. A. Eppler's and G. H. Spencer-Strong's investigations[240] of the role of *phosphates* (P_2O_5) in TiO_2-opacified porcelain enamels, and how the reflectance and color tint then are influenced. When it was postulated by R. D. Shannon and A. L. Friedberg[241] that P_2O_5 would retard, or even *impede* the anatase → rutile inversion, the X-ray diffraction-analytical data presented by Eppler *et al.* spoke *against* this hypothesis. In the range between 0.5 and 4.0% P_2O_5 concentration in frits, the rates of crystallization for both modifications of TiO_2 are increased in the ratio 2:1 for anatase/rutile. In every case, P_2O_5 appears to be a strong catalyst for the crystallization of anatase; it accelerates by a factor of 4:1 in a concentration of 4%, but much less for the crystallization of rutile. The difference in both reactions may be responsible for the observed changes in reflectance and color tint when P_2O_5 is present in different concentrations in the products of the experiments of Shannon and Friedberg.

[239] Cf. *Acta Chem. Scand.* **12**, 951–958 (1958); **14**, 1654–1659 (1960).
[240] *J. Amer. Ceram. Soc.* **52**, (5), 263–266 (1969).
[241] *Univ. Illin. Eng. Exp. Sta. Bull. No.* 456, 60 pp. (1960).

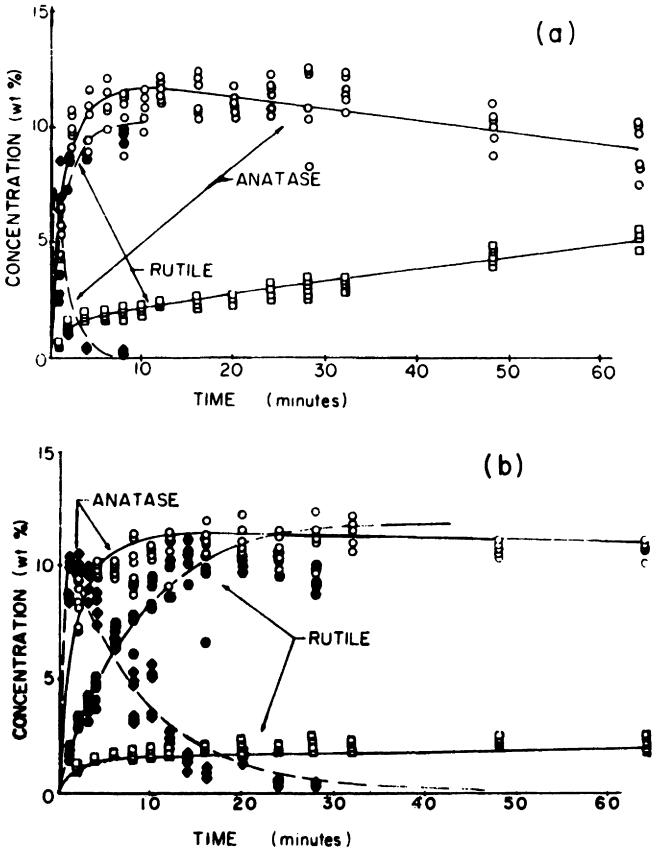


FIG. 143. (a) Rutile and anatase concentrations in enamels fired at 940°C (solid symbols) and 780°C (open symbols). (b) Rutile and anatase concentrations in enamels fired at 800°C (solid symbols) and 660°C (open symbols). (Eppler.)

TITANIUM, TIN, AND ZIRCONIUM DIOXIDE-OPACIFIED ENAMELS AND GLAZES

644. A special examination of the reflectance phenomena in *titania*-opacified porcelain enamels made by R. A Eppler[242] discusses the problems more from the aspect of technological practice. With application of G. Mie's theory of light scat-

[242] *Bull. Amer. Ceram. Soc.* **48**, (5), 549–554 (1969).

tering, the amounts of crystalline phases present could be determined; practice in a maximum effect is reached for a crystalline TiO_2 concentration of about 15%. The additional parameters of particle sizes are demonstrated by impressive results published by W. H. Engel, R. A. Eppler, and D. W. Parsons[243] who applied electron microscopy in transmitted radiation, using the thin-section techniques of sample preparation. Rutile is striking in the micrographs for its acicular morphology, anatase showing prevailingly more cube shapes or rectangular forms, and star-shaped aggregations below 720°C as the firing temperatures. The average particle size in such samples is increased to 895°C. The range of the particle sizes was found normally within $\pm 0.1\sigma$ (standard deviation σ); the mean size is typically 3:1 to 4:1; contrary to common interpretation, all acicular particles are *not* rutile, some are anatase.

645. R. A. Eppler[244] demonstrated how to apply the theory of optical scattering phenomenon by dispersed particles to the evaluation of the reflectance spectra of TiO_2-opacified porcelain enamels, namely, by preparing specially thinned sections for electron microscopy to study the scattering mechanisms in a given dispersoid system. Particle sizes calculated from the mathematical formulations of the scattering theory agree very well with direct information verified by electron microscopy in transmission techniques, in the case the particles are so close that they act optically as single ones. The standard deviations from the theoretical distributions are lower than those experimentally found. It is highly interesting to see how Eppler applied the *mechanical thinning* techniques which we discussed in Vol. VI.C. ¶ 194 ff., 205 ff. to obtain samples of only 1000 Å in thickness. The logarithmic normal distribution function could be used for the evaluation, when conventional assumptions can be made on corrections of counting in the electron micrographs of all the crystallization products which appear to touch in those, as *single* crystals. As a matter of fact, most of the distributions are log normal, but single exceptions may occur, probably when agglomeration must be assumed, or star-shaped clusters are visible, mostly in shortly fired ceramics samples in which the "severity" in firing is in question.

646. Speaking of the reflectance of enamels and glazes as a function of microstructural particularities, we may conclude by citing a very recent investigation by M. D. Dennis and R. C. Bradt[245] of the crystalline opacifiers TiO_2 or SnO_2, but also ZrO_2 and $ZrSiO_4$, in a lead borosilicate glass which showed a primary opacity by liquid/liquid phase unmixing and separation of droplets, in one distinct concentration area of the ternary system $PbO-B_2O_3-SiO_2$. In this case, not only are additions

[243] *Bull. Amer. Ceram. Soc.* **49**, (2), 175–179 (1970).
[244] *J. Amer. Ceram. Soc.* **54**, (2), 116–120 (1971).
[245] *J. Amer. Ceram. Soc.* **54**, (5), 232–235 (1971).

of crystalline opacifiers, as system-foreign ingredients in the microstructure of the glass playing the normal role of turbidity agents, but an intrinsic liquid phase unmixing mechanism is acting in basic cooperation with the evolution of reflectance effects. The maximum reflectance then results from a balance of the effect of highly differing refractive indices of the added oxides or silicates, relative to that of the matrix material, but reinforced by the droplet microstructure as such. A fine-droplet texture in the electron micrographic image indicates the essential reason for this latter "opacifying" effect. In this respect also, the maximum reflectance effects of mixed opacifier agents are of a high practical interest that in materials containing such relatively inert opacifiers as SnO_2 and $ZrSiO_4$ (cf. Fig. 144) show an *enhanced* reflectance over the entire visible spectrum. Interesting is the decrease of reflectance beyond the enhancement maximum in those curves which is directly related to an onset in the breakdown of the optimum liquid droplet immiscibility microstructures. The summary effect of percentage opacifying oxides (like SnO_2, ZrO_2) alone, and in their mixtures, is well demonstrated by Fig. 145.

647. Another, pyrochlore-type compound which plays a certain role as a yellow-colored Pb – Sn oxide opacifier in ancient glasses, was described by H. P. Rooksby[246]; it could be synthetically prepared by a solid-state reaction of lead stannate, $PbSnO_4$, and silica at 800° to 950°C. The crystal structure is that of $Pb_2Ti_2O_7$, $Pb_2Sb_2O_7$,

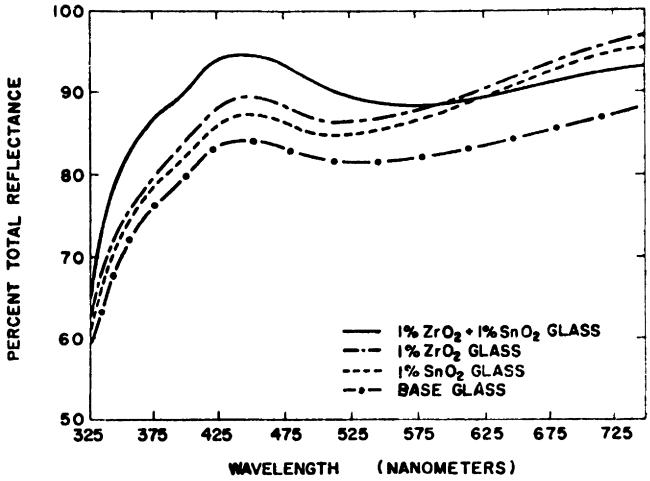


FIG. 144. Reflectance of compositions quenched from 850°C, showing reflectance enhancement and change in energy distribution. (Dennis and Bradt.)

[246] *Phys. Chem. Glasses* **5**, (1), 20–25 (1964).

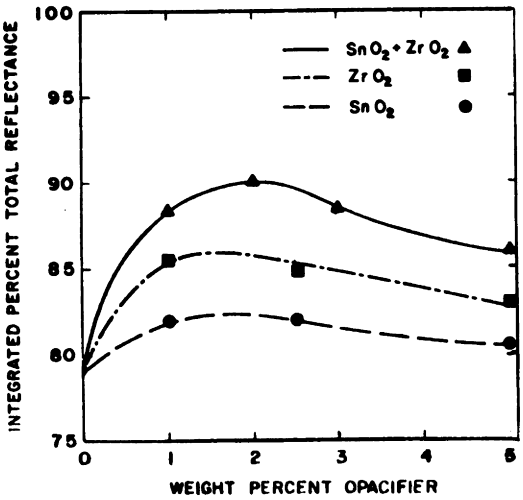


FIG. 145. Integrated Reflectance of tin dioxide and zirconia compositions quenched from 800°C. (Dennis and Bradt.)

$Pb_2Nb_2O_7$, and of the minerals of the F-containing *atopite*, $NaCaSb_2O_6F$, as indicated above. The analytical composition of Rooksby's lead–tin–silicate is about $Pb(Sn \cdot Si)O_3$, but $Pb_2Sn_2O_7$ is pronouncedly unstable as is $Pb_2Ti_2O_7$ of pyrochlore structure, with a rapid and complete loss of its rich yellow color, although all of its quality as an opacifier is not destroyed and indeed, may be restored by adequate reheating. In every case, these observations supplement many of those made with the perowskite–pyrochlore-type changes and conform with the highly fascinating problems of the constitution, structure, and properties of this double-group of minerals.[247]

648. The role of *tin dioxide* as an opacifier agent in silicate glasses and glazes was investigated by J. Carbó Nóver and J. Williamson,[248] in a study of the partial system $SnO - SiO_2$. Below 700°C, the compound $SnSiO_3$ crystallizes; it is dissociated again when heated above this temperature, until SnO is finally disintegrated to Sn metal and SnO_2. This latter reaction makes evident how an SnO-containing glass devitrifies under the temperature conditions of industrial glass furnaces and shows

[247] See also E. Aleshin and R. Roy, *J. Amer. Ceram. Soc.* **45**, (1), 18–25 (1962); cf. ¶ 634* Footnote 228 from which we take the instructive Fig. 140 to show the correlation of the pyrochlores to CaF_2 and $CaTiO_3$ perowskites.

[248] *Phys. Chem. Glasses* **8**, (4), 164–168 (1967).

on its microscopic image a precipitation of droplets enriched in tin, associated with acicular crystals of SnO_2 (cf. Vol. III.B. ¶ 417).

649. Mössbauer spectra to *tin dioxide-opacified glasses* were studied by K. P. Mitrofanov and T. A. Sidorov,[249] with the understandable conclusion that there is no direct agreement with the simple assumption of an at random disordered framework structure of such a glass, but that definite chemical bondings to form well-defined chemical compounds rule. Sidorov, V. A. Tyul'kin, and K. P. Mitrofanov[250] supplemented the Mössbauer examinations by measurements of the electron paramagnetic resonance, and nuclear γ-resonance effects in glasses of the system $Na_2O-SnO_2-SiO_2$, which give a positive answer to the coordination problems for Sn^{4+}; it is doubtless octahedral, but the presence of Sn^{2+} ions restricts the development of hole centers at the nonbridging oxygen atoms when the glasses are subjected to ionizing radiations.

650. In analogy with the opacifying effects of finely dispersed particles of TiO_2 and SnO_2, which have long been highly valuable in the production of white enamel and glaze coatings in ceramic technology, the role of *zirconia* is still in evolution. H. Oel, H. Lachenmayr, and A. Dietzel[251] presented a comprehensive report on extensive chemical, microscopic, and X-ray diffraction-analytical studies for commercial glaze frits matured at 1040° to 1050°C, fired onto ceramic and experimentally onto platinum sheet, and powder enamels fired at 850° to 950°C on cast iron. During "gloss" firing, zirconia reacts with silica from the silicate melt to precipitate $ZrSiO_4$ as the main opacifier agent, and some metastable cubic ZrO_2 as temporary constituents of the glaze mixtures. The opacity is caused less by coarser than by finer particles; the finer ground the ingredients, the better the opacifying effects. Optimum firing temperatures are determined by the proportional amounts of finest and coarsest suspended particles of the Zr compounds present in the frits. A uniform degree of fineness in grain size distribution prevents the well-known overfiring anomalies. Addition of alumina promotes, in any case, a secondary crystallization of $ZrSiO_4$. In enamels, the simultaneous presence of CaF_2 and ZrO_2 may be essential for the desirable degree of whiteness. The often made observation that in the lower parts of a glaze layer show a higher degree of opacity than in its upper portions, is assumably an indication that the ceramic body enhanced the intensity of the opacifying and whitening effects. From practical viewpoints, we may cite the excellent report given by Bh. Bhushan and S. Sen[252] on the recent standard of experimental and theoretical studies of the zircon glazes, their intrinsic properties, and the mechanisms of opacifi-

[249] *Fiz. Tverd. Tela* **9**, (3), 890–894 (1968).
[250] *Zh. Strukt. Khim.* **9**, (3), 440–444 (1968).
[251] *Ber. Deut. Keram. Ges.* **42**, (12), 462–467 (1965).
[252] *Centr. Glass Ceram. Res. Labor. Bull* (*Calcutta*) **12**, (2), 71–76 (1965).

cation, combined with very important information on India's resources of zircon and zirconia, and their economic importance.

651. Differences in the significance of fully homogeneous glasses and industrial glazes were examined by K. Beyersdorfer[253] in the well-known technological application and aftertreatment processes, as well as the deep-going differences in the reaction mechanisms of corrosion exerted by their melts on refractories and the porcelain substrates. The absolutely preponderant application of *opacified* frits, enamels, and glazes—in contrast with homogeneous glass—puts into the foreground the role of opacifying oxides, fluorides, and a few other groups of chemical reagents. But, deep-going differences are also evident in the degrees of rheological and viscosity characteristics which are fundamental for the manufacturing processes in both branches of ceramic industries; it is fascinating to see the significance of those differences at work in the colloid-physical principles of dispersoid techniques in one branch, and hydrodynamic and -static viewpoints in the other. For both branches, the physical principles and chemical qualities in the presence of color centers are most evident for the entire field of applied optics and spectroscopy.

652. *Zircon dioxide*-containing glazes have a notorious tendency to develop "pinpricks" e.g., in wall tiles. These pinpricks have been repeatedly studied for their effects and their correlation to fundamental properties of glazes, chiefly their viscosity, surface tension and the constituents from which the frits are prepared, and for many other variables, not to speak of wide differences in technical factors and conditions under which such highly undesirable phenomena appear. All the variables have been carefully examined and critically discussed anew by H. W. Hennicke, H. E. Schwiete, and A. Reiss,[254] starting from previous tests made by microscope (cf. ¶ 309) which attribute the pinpricks to the elementary formation of gas evolution in glass melts in batch reactions and fining seeding (cf. ¶ 115) in different physiognomies as made by A. Schoblick,[255] and in rich, more recent literature, such as the publication by P. Azarov, G. V. Berdova, and S. B. Grechanova.[256] These confirm older experiences of glass technology that the viscosity of defects from "pinholing" may be reduced or even eliminated by carefully avoiding any overfiring schedule in crystallization practice, which would promote the intensity of gas evolution from oversaturated melt solutions.

653. The rich numerical data on measurements of the fundamental temperature functions of viscosity, density, and surface tension make it evident not only that

[253] *Glastech. Ber.* **38**, (9), 364–368 (1965).
[254] *Sprechsaal* **98**, 302–315 (1965).
[255] *Sprechsaal* **84**, 165–168 (1951).
[256] *Silikattechnik* **10**, (4), 187–189 (1959).

the temperature of glazing should be kept as low as possible, but also that there is an optimum efficiency of those measures for the logarithm of viscosity, (log η = about 5.5). In addition, it is very important that conclusions are made from quantitative X-ray diffraction measurements of the opacifier (mostly $ZrSiO_4$ introduced as mineral zircon crystallization) which confirm the close correlation of the mechanism and degree of specification with the intensity degree of pinpricking in the glaze melts. It is rather self-evident that one should keep the gas content of the frits as low as possible, and enhance an early degassing in order to avoid the troublesome late-bubbling. For the control of viscosity at moderate temperatures (800° to 1800°C), namely, in the range from $\eta = 10^{2.5}$–$10^{7.0}$ torrs, the use of a simplified indentation device recommended by W. James and S. N. Norris may be particularly helpful[257] primarily as shown in Vol. II.B. ¶ 265 (see, e.g., page 563).

654. To determine the *solubility* and crystallization of zircon from glazes for sanitary ware and wall tiles, K. H. Karsch[258] studied an *orientation* of the early crystal development with the (100) face parallel to the surface of the smooth glaze. The number of such tabular crystallites depends on the kiln atmosphere and on variable degrees of *solubility* of $ZrSiO_4$ in the glaze melt in which they may act as nucleating centers for additional crystal growth. In melts of Pb borate glazes, the orientation effects observed are much more pronounced than they are in common glazes for wall tiles and sanitary ware; the solubility is then about double that in common zircon glazes; in tin dioxide-containing glazes, the solubility may be even notably higher. Karsch explained the occurrence of the crystallographic orientation of zircon crystallites parallel to (100) not only by the usual solubility factors,[259] but chiefly by nucleation effects exerted by residual fragment material from ball milling of the zircon raw material concentrates before they are added to glaze frit batches, and before their (incomplete) dissolution. A satisfactory degree of opacity is achieved only when the minimal concentrate has a grain size between 1 and 15 μ in diameter.[260]

655. High-temperature X-ray diffraction analyses of different $ZrSiO_4$-containing glaze frits were made recently by K. A. L. Sehlke and A. Täuber[261]; it makes

[257] *Trans. Brit. Ceram. Soc.* **55**, (11), 601–630 (1956), specifically pp. 606 ff.

[258] *Ber. Deut. Keram. Ges.* **44**, (9), 440–444 (1967).

[259] Cf. G. R. Rindone, Symp. on Nucleation and Crystallization in Glasses and Melts, pp. 63–69, Amer. Ceram. Soc. Columbus, Ohio, 1962; see also R. F. Hochman and I. D. Fleming, *J. Amer. Ceram. Soc.* 47, (2), 104 (1964).

[260] Cf. E. Tauber, *Aust. Nat. Clay* **6**, (9), 8–10 (1965), who described a special injector mill for this purpose; on the use of zircon in the ceramic industry, in general, cf. E. Tauber and R. J. James, *J. Aust. Ceram. Soc.* **7**, (2), 27–33 (1971); cf. V. B. ¶ 165 ff. with valuable literature references.

[261] *Trans. Brit. Ceram. Soc.* **68**, (2), 53–56 (1969).

remarkable differences in the mineral composition of the crystalline Zr silicate products when frits are compared which, in spite of similar ratios $ZrO_2:SiO_2$ have different compositions of the glassy matrix substance of the frits. Sehlke and Täuber come to the conclusion that not only $ZrSiO_4$ is present in frits containing $ZrSiO_4$ in the form of the zircon as the mineral but that the silicate is practically associated every time with ZrO_2 usually in its monoclinic modification, but that $ZrSiO_4$ is much easier dissolved in frit melts than is ZrO_2. Besides the monoclinic ZrO_2 (as mineral baddeleyite) the tetragonal modification (tentatively called "ruffite") was identified in the X-ray diffraction diagrams of frit samples exposed to a maturing temperature of 1000°C (cf. Fig. 146, to show the very characteristic behavior of such frits when PbO is introduced). The quantitative amounts of those three crystal phases may vary over rather wide ranges, as a function of special thermal treatments by which increasing "soaking" time periods provoke increasing portions of $ZrSiO_4$, but less ruffite. Addition of PbO to the frit composition decreases the viscosity of the resulting melts, and accelerates the rate of the reaction $ZrO_2 + SiO_2 \rightarrow ZrSiO_4$, stabilizing the tetragonal modification. H. Jürine[262] emphasized that tetragonal, metastable ZrO_2 is the opacifying crystal phase of some glazes, being inverted to the monoclinic modification and finally, by reacting with silica, to zircon. Small changes in the ratio ZrO_2/SiO_2 may be critical for the amounts of the different crystal phases, in the same way that PbO, Al_2O_3, B_2O_3, alkalies and alkaline earth oxides act. It is of practical importance also that the refractive index of baddeleyite (2.19) is higher than that of zircon (1.923) for the degree of opacity of the Zr glazes, the refractive index being reduced by silica in the matrix glass.

656. Coming back to the problems of bubbles containing entrapped gases in glost-fired glazes, A. C. Bersticker, B. J. Sweo, and J. D. Snow[263] (cf. ¶ 200) made evident that nitrogen is the principal gas in the bubbles when the firing is done in air, evidently due to dissolution and absorption of oxygen into the melt. Nevertheless, mere diffusion is only a minor factor in bubble formation, although it is convincing that diffusion of dissolved gases plays a certain role in the complex phenomena of blistering. Mere adsorption of gases on the surface of particles suspended in glazes can also not be a major factor in the evolution. *Deuterization* of experimental glaze frits was done in the commonly used process of milling; application was made on platinum sheet, and glost firing in steps in an atmosphere of pure argon. By this procedure, it was definitely established that the entrapment and dissolution of gases is the principal source of bubbles which, in these experimental glazes were

[262] "Science of Ceramics," Vol. I. pp. 35–49, Academic Press, New York, 1962.
[263] *Bull. Amer. Ceram. Soc.* **45**, (11), 1009–1011 (1966).

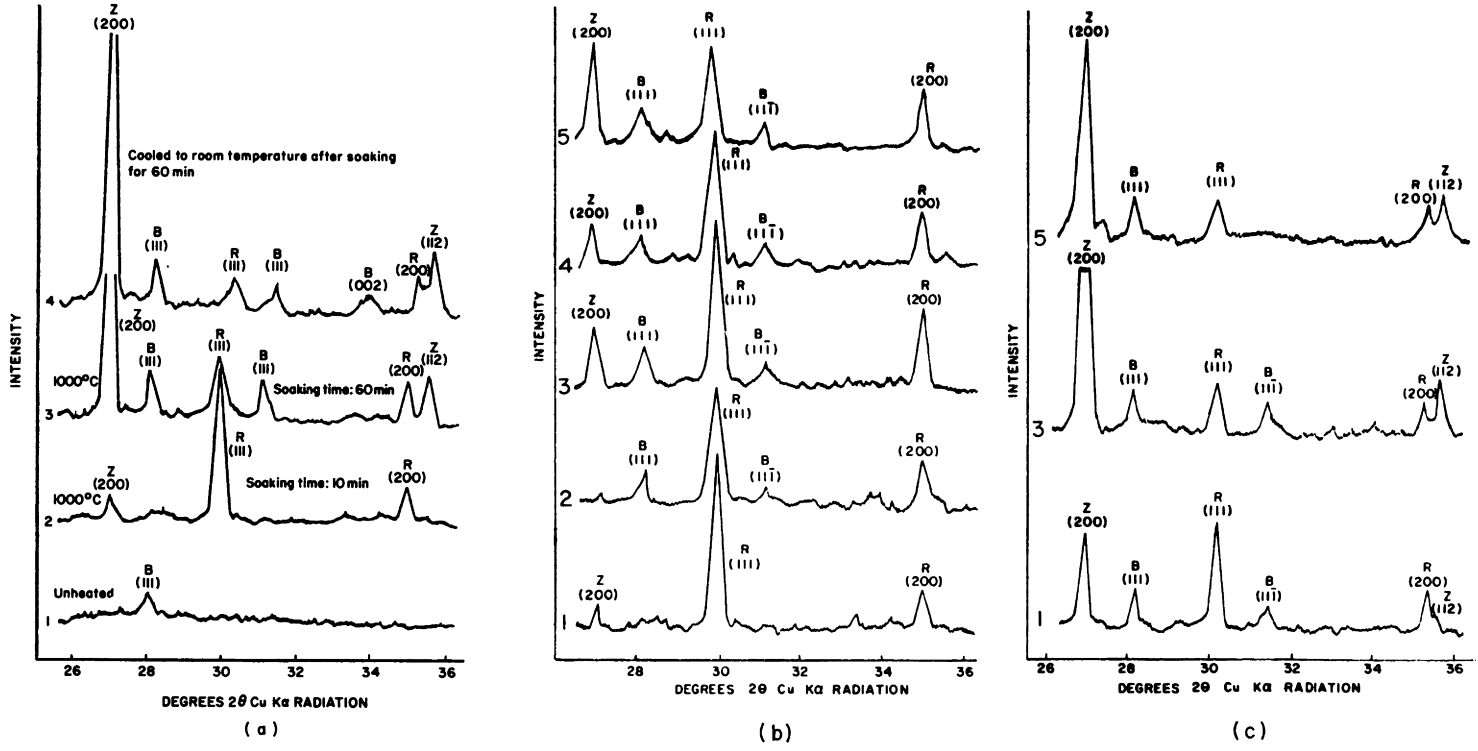


FIG. 146. X-ray diffraction diagrams of an alumino-borosilicate frit "B" [(a) composition with 5 mole % Al_2O_3; 19.6 mole % B_2O_3; 7.1 mole % K_2O; 1.8 mole % SrO; 7.0 mole % ZrO_2] to which increasing amounts 0.5 mole % (b) and 2.5 mole % PbO (c) were added. (Sehlke and Täuber.) The diffraction diagrams make impressive considerable changes in the amounts of crystalline phases [Baddeleyite (*B*), Ruffite (*R*), and Zircon (*Z*)], after different thermal treatments.

found by mass spectrometric analysis to contain D_2O. The question still open to a certain degree, is whether or not the ceramic substratum, namely, the "bisque" glaze, or the ceramic body *per se*, are participating in the entrapment reactions, although it is evident that an entirely inactive substratum like Pt sheet did (in argon atmosphere) *not* interfere as an entrapping medium; the possibility, or even necessity, for evolution of bubbles and "seeds" is therefore excluded, restricting the possible sources by entrapment in the glaze. Samples prepared from glaze batches, milled, fritted, and applied in argon, but glost fired in helium atmosphere, later contained exclusively helium, but no argon, in their gas bubbles, as again established by mass-spectrometric measurements and gas analysis.

657. *Plasma-sprayed* glassy enamels have, according to A Krauth and H. Meyer[264] a quite specific interest also from the practical viewpoints that the system SiO_2-ZrO_2 was not yet known as a glass-forming one; however, it is convincing that in the plasma-sprayed melts, a concentration range is observed in which well-defined and homogeneous glasses occur which have a low viscosity, and build up layer coatings with good coherence. Beyond that, the technological character of flame-sprayed $Al_2O_3-ZrO_2$ glasses is of great interest; in such glasses the coordination $[AlO_4]$ indicates the typical *aluminate* character of the material involved, of densities between 4.00 and 4.33, a thermal expansion coefficient between 58 to 70×10^{-7} per °C, i.e., 65 to 70×10^{-7}°C as the difference between the expansion coefficients of steel and the aluminate layer of notable thermal shock resistivity, a very low permeability for gases, and a high spalling and chemical durability, which is ideal for coatings required in the chemical industry. Glassy layers of related composition, containing besides ZrO_2 and Al_2O_3, MgO and CaO, have even a better mechanical protection effect than crystalline coating layers, in general, may show. All this is in remarkable contrast with other plasma-sprayed layers of high viscosity which are *not* promptly coalescent, but build up agglomerations of spherical particles.[265]

658. H. Krauth and H. Meyer extended their studies on plasma-sprayed refractory oxides and their binary and ternary systems with SiO_2, Al_2O_3, $ZrOCl_2$, and ZrN in combination with ZrO_2[266] in which ZrO_2 appears as the tetragonal high-temperature modification after sudden quenching, when the crystallites are very small. Larger crystals have the structure of the energy-poorer monoclinic type. In the system ZrO_2-SiO_2, no crystallization of SiO_2 could be observed, but above

[264] *Mitt. Ver. Deut.* Emailflachleute **14**, (1), 1–4 (1966).

[265] On the crystallization behavior of flame-sprayed ZrO_2 and mixtures of the system $ZrO_2-Al_2O_3$. see also III.A. ¶ 62, footnote 87; III.B. ¶ 400, footnote 600.

[266] *Ber. Deut. Keram. Ges.* **42**, (3), 61–73 (1965).

20 mole % SiO_2 tetragonal crystals of ZrO_2 are formed. Mixtures of the system ZrO_2-ZrN show a tendency of the nitride to oxidation to ZrO_2; only by very rapid quenching is it possible to preserve crystalline ZrN besides tetragonal and monoclinic ZrO_2. Evidently, the two modifications of ZrO_2 have much different surface energies[267]; inversion of tetragonal ZrO_2 crystallites to the monoclinic modification takes place, as a rule, when they reach a size of more than 170 Å in diameter.

Some interesting ideas on a possibility that there can be useful developments of transparent and/or opacified glasses in the system $MoO_3-Na_2O-SiO_2$ were discussed by E. Rykiert,[268] with some orienting experimental and structural data from microscopy and X-ray analysis.

[267] Cf. III.A. ¶ 82, footnote 115.

[268] *Szkt. Ceram.* **19**, (34), (7), 193–196 (1968).

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