

4. Cupric copper is reduced to cuprous copper fairly rapidly by carbon monoxide, but the reduction of cuprous copper to copper is comparatively much slower. Oxygen present in small amounts, in gaseous mixtures from which carbon monoxide is to be removed by absorption, will prevent the precipitation of copper and increase the absorption capacity of the solution.

5. Practically complete removal of carbon monoxide from used cuprous ammonium carbonate solutions can be effected by heating to 75° at atmospheric pressure in an inert atmosphere, without decreasing the absorption capacity of the solution.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY.]

THE DEVITRIFICATION OF GLASS, A SURFACE PHENOMENON. THE REPAIR OF CRYSTALLIZED GLASS APPARATUS.

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It has generally been supposed that the devitrification of blown glassware in storage or in daily use is a phenomenon similar to that studied by Tammann,¹ Guertler² and others, which depends on the tendency of a supercooled liquid to form crystal nuclei, from which crystallization proceeds. Tammann showed that spontaneous devitrification depends on 2 factors, which seem to be related to the viscosity of the supercooled liquid: the tendency to form crystal nuclei, which increases with the degree of supercooling, though the rate at which nuclei have been observed to form reaches a maximum, and then on account of the damping effect of the diminishing temperature on the speed of formation, rapidly decreases and for most glasses reaches a value of zero at room temperature; and the speed with which crystallization proceeds from the crystal nucleus, which for commercial glassware also reaches a value of zero for ordinary temperatures. Tammann has shown that certain substances in solution act catalytically on the formation of crystal nuclei, and that in certain instances the rate may be depressed to zero even in the temperature range of the maximum. This is evidently the ideal condition for chemical glassware, a condition more or less successfully achieved by glass manufacturers.

It has also been shown³ that by repeated fusion and solidification supercooled liquids which otherwise devitrify readily can be obtained in the vitreous state. In all cases of this sort that have been studied water

¹ Tammann, *Z. Elektrochem.*, **10**, 532 (1904).

² Guertler, *Z. anorg. Chem.*, **40**, 268 (1904).

³ See Herbert Jackson, *Chem. News*, **120**, 62 (1920).

vapor is given off progressively during the process of fusion, and with the removal of it the vitreous state has been found to persist more and more. Subsequent re-introduction of water has been found to promote crystallization. Herbert Jackson is responsible for the statement that the conclusion seems to be justified that water, and to a smaller extent carbon dioxide, act chemically when many glasses are heated in flames, and that this action plays an important part in the initial stages at least of devitrification. This is undoubtedly true, for it is known that certain glasses, which devitrify very readily in the gas flame, can be worked if heated by radiation. A glass containing barium oxide, which was very stable when heated by radiation in a muffle furnace, quickly devitrified in a gas flame, first becoming grey; under the microscope the grey appearance was shown to be due to the separation of minute bubbles, apparently caused by rapid absorption and subsequent evolution of gases.¹

Splitgerber² relates his experience with a bit of glass at least 10 years old (most chemists will recall similar experiences): the lenses from a pair of glasses had to be reset, and during the process were heated over a spirit lamp; the surface became roughened and as if frosted over. He showed that this was caused by the driving out of moisture from the glass surface, moisture which was chemically combined. This behavior is not given by a fresh surface, for a piece whose surface had clouded on heating was ground down and polished, and when again heated showed no clouding.

It has often been noted that glass, under certain conditions, shows efflorescences of sodium hydrogen carbonate on its surface; I have preserved a number of unused test-tubes, imported from Germany before 1914, each of which shows such efflorescences. These tubes all show a marked tendency to devitrify when heated.

It is possible to explain devitrification of chemical glassware as a purely surface phenomenon, unrelated as to immediate causes to the phenomena observed by Tammann.

Much has been said about the surface film of moisture on glass which has come to equilibrium with the atmosphere, but the tremendous affinity of glass for moisture is nevertheless too little appreciated; let me recall an observation made by Moissan that ought to be better known.

"The affinity of dry glass for moisture is so great that carbon dioxide saturated with water vapor at -20° must be passed (through a tube of dry glass containing sodium hydride) for several hours before the gas reaches the hydride in a moist condition."³

The silicates of which the glass is composed are in equilibrium with this water, and must be more or less hydrolyzed, depending on the composi-

¹ H. Jackson, *loc. cit.*

² Splitgerber, *Pogg. Ann.*, **82**, 453 (1851).

³ *Compt. rend.*, **136**, 723 (1903).

tion of the glass, so that we may assume the presence of silicic acid, calcium hydroxide and sodium hydroxide; the bases, however, absorb carbon dioxide from the air, and so are converted to the hydrogen carbonates. The efflorescence is thus directly explained. Washing removes most of these carbonates. Heating, however, drives off adsorbed moisture, dehydrates the silicic acid, and roughens the surface, depending on the extent of the "weathering" of the glass. The separated silica forms an infusible coating over the surface of the glass, which may under certain conditions dissolve in the underlying silicate, and the surface clear up, or under other conditions yield difficultly fusible calcium silicate, in which case well defined crystal surfaces may appear,¹ the subsequent phenomena being closely similar to the devitrification studied by Tammann and by Guertler, except that crystallization proceeds from the surface, and not from crystal nuclei on the interior of the mass.

To test the possible correctness of this view, the surface of a tube that had become badly devitrified before the blowpipe was carefully washed with dil. hydrofluoric acid, to remove the separated silica from the surface, and an attempt was again made to work the glass in the flame. The result was remarkable, but entirely in keeping with the hypothesis; as the glass reached the softening point, it became perfectly clear, and could be blown as well as the best new glass. The same result was attained by removal of the surface layers by washing with dil. hydrofluoric acid before heating the glass in the flame, so avoiding any tendency towards devitrification.

At the same time the older hypothesis that sodium oxide is slowly volatilized by long continued heating of glass near its softening point must not be lost sight of, for glass which shows no initial tendency to devitrify does so if kept in the flame too long. A common practise has been to reintroduce the lost alkali by some method, but this is always difficult to do. Treatment with hydrofluoric acid, however, is very simple, and thoroughly effective.

At the Morley Laboratory we have had some difficulty during the past few years in obtaining suitable glass for constructing apparatus for work with gases. Much of Professor Morley's apparatus remains, but practically all of it devitrifies when the effort is made to work it in the flame. With the new method, however, all of it at once became available for use. Five advanced students, working on various phases of the physical chemistry of pure and mixed gases, each of whom has had to construct his own apparatus, have been able to work without fear of loss through devitrification, which has always been a source of much annoyance to beginners in the art of glass blowing.

¹ I have preserved a tube of heavy glass which, when heated, developed into what appears to be an excellent example of this sort.

If the devitrification of glass were dependent upon the formation of crystal nuclei upon the surface or within the mass of the glass, a cool storage space would seem to be ideal; my experience has, however, been that glass which had been stored in an attic room under a slate roof for 15 years showed less tendency to devitrify than another lot stored in a ground floor room of our reinforced concrete laboratory for 5 years. This is perplexing unless we admit that devitrification depends upon absorption of moisture; the atmosphere of the laboratory has an average humidity much higher than the atmosphere of the attic room, which is in another building. Certain gases present in the atmosphere of a chemical laboratory also seem to play a part, probably acting catalytically; halogen gases, except those containing fluorine, for obvious reasons, seem especially active in this way. A tube which had contained phosgene devitrified badly before the blowpipe; the same tube, after having been exposed casually to the laboratory fumes for more than 6 months, no longer showed any tendency to devitrify.

Summary.

That the devitrification of glass before the flame is a surface phenomenon is shown by the fact that the tendency to devitrify may be removed by rinsing the parts to be fused with dil. hydrofluoric acid, thus removing the surface. Old apparatus which has been broken may be repaired by taking advantage of this fact.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GRINNELL COLLEGE.]

THE ELECTRO-TITRATION OF HYDRIODIC ACID AND ITS USE AS A STANDARD IN OXIDIMETRY.

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The determination of the iodine ion when not associated with chloride or bromide is simple and accurate, gravimetrically as silver iodide, volumetrically by the Volhard method; but, when mixed with either of the other halogens or both, as it is likely to be, its determination is difficult and this has formed one of the perennial problems of analytical chemistry for nearly a century. The literature contains, of course, a large number of varieties of methods for the volumetric determination of iodides, but they can be reduced to a few clearly marked types. Special citations here seem unnecessary since the whole subject is being worked out, reviewed and criticised by I. M. Kolthoff,¹ under the general title "Iodometric Studies."

¹ Kolthoff, *Pharm. Weekblad*, **56**, 391, 572, 878, 1322, 1466 (1919); **57**, 53, 82 (1920); cf. *Chem. Abst.*, **13**, 1434, 1569, 3103 (1919); **14**, 34, 504, 1270, 1271 (1920).