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Hydrogen evolution in fused quartz ampoules

J. J. MURRAY, R. F. POTTIE, R. L. SANDER
Division of Chemistry, National Research Council of Canada, Ottawa, Canada

Using a mass spectrometer it has been shown that up to 4×10^{-6} litres at s.t.p. of hydrogen per cm^2 of surface are irreversibly evolved in evacuated fused quartz ampoules at 1300K after normal degassing. Fused quartz of various types and from various sources has been tested for this effect. The contribution of this gas evolution to sample contamination during phase preparation, annealing, etc. is discussed. A thermal pretreatment procedure which reduces the hydrogen evolution by approximately a factor of forty has been devised.

1. Introduction

In the study of many inorganic solids, fused quartz (transparent vitreous silica) is used to encapsulate the materials *in vacuo* or in inert gas for phase preparation, annealing, the preparation of single crystals by sublimation or vapour transport, etc. Fused quartz of the standard or commercial grade (see below) is usually used and provided that reaction of the sample with the glass does not occur, sample contamination is considered negligible. Possible contamination by the gases evolved from the glass upon heating is generally allowed for by degassing at 500 to 600 K prior to closing the ampoule. This process does reduce the amount of water evolved after the ampoule is sealed. Any gases released after the degassing may be incorporated into the phase being prepared and significant physical property changes may occur, particularly if repeated processing in such ampoules is necessary.

Three basic types of fused quartz are available commercially. They differ as to mode of manufacture, OH group content, metallic impurity level and physical properties [1]. Standard or commercial grade fused quartz (approximately 150 ppm OH, 20 ppm metallic impurities) is made by the fusion of quartz crystals or silica sands in a flame, usually a H_2–O_2 flame or at least in an atmosphere containing hydrogen. Optical grades with a low OH concentration (<5 ppm OH, 50 to 100 ppm metallic impurities) are made by vacuum fusion of quartz crystals or silica sands. Optical grades of high purity (< 1 ppm metallic impurities, up to 1200 ppm OH) are generally synthetic fused quartz made using reactions of the type

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl\,.$$

Synthetic fused quartz of low OH content is also available. More and larger gas bubbles and "airlines" are present in the standard grade than in the other grades. Since the standard grade is readily available in the form of tubing and is significantly less expensive than the other grades, it is commonly used to fabricate the ampoules, manifolds etc., used as described above.

During several investigations in this laboratory, sample contamination did occur when ampoules made of a standard grade fused quartz were used. The present study was made to establish the origin of the contamination and to reduce or eliminate it. Techniques for the analysis of gases in glasses are well known [2]. The technique of heating the glass *in vacuo* to release the gases has been superceded by techniques of sampling a single bubble and analysing its contents [3, 4]. Such work is largely limited to various low temperature glasses, the object being to eliminate the bubbles in the glass.

In the present work only those gases which are evolved upon heating *in vacuo* are of importance and thus the heat-release technique was employed.

2. Experimental

The measurements were made using an Atlas CH-4 mass spectrometer which was equipped with a micromanometer in the inlet system capable of measuring 2 μm pressure with an accuracy of ± 10% (± 1% at 20 μm and above).

An ampoule 15 cm long by 1 cm i.d. with a break seal at one end was made from the fused quartz tubing and evacuated to at least 10^{-6} torr with thorough flame degassing at $\simeq$ 600 K. After being closed by sealing using a flame, the ampoule was heated in a tube furnace at 1300 K for 2 h and air-quenched. Following thorough pump down of the manifold and inlet, a blank scan was made according to the same procedure and time schedule as for a sample scan, except that the break seal was not opened. To analyse the sample, the seal was broken allowing the gases in the ampoule to enter the manifold. These gases were then expanded into the spectrometer inlet where the pressure was measured. Using the volumes of the inlet and the manifold which had been previously determined by gas expansions from standard volumes and the estimated volume of the ampoule, the original pressure in the ampoule was calculated using the ideal gas law. The sample was then admitted through a molecular leak directly into the ion source. The sensitivity was checked regularly for H_2 and CO_2 and occasionally for CO, N_2 and CH_4 as well. Some fifty samples were analysed using different fused quartz materials, fabrication flames, pretreatment procedures and degassing procedures.

3. Results

The results are summarized in Table I for fused quartz subjected to the test procedure described above except as noted in the table. The results of many replicate experiments are not included. Three sources of fused quartz were used, Amersil Inc, General Electric Lamp Glass Division and the US Fused Quartz Company. Glass identification numbers, as defined in the footnote to Table I, are used here since specific identification of source is not intended. The pressure of gases in the ampoules was in the range 10^{-2} to 13 torr. These values were converted to litre-cm^{-2} (s.t.p.) by estimation of the interior surface area and volume of the ampoule. For the low pressure samples, $< 1 \times 10^{-7}$ litre-cm^{-2} (s.t.p.), the analysis is complicated by instrumental background interference, especially at $m/e = 28$ for both CO and N_2. Hence the relative proportions of CO and N_2 are subject to considerable uncertainty, particularly in the presence of CO_2.

Experiments 1 and 2 were blank experiments

TABLE I Analysis of gases evolved at 1300 K from fused quartz

Experiment no.	Glass*	Pretreatment (K)†	Working flame‡	Gas evolved Litre-cm^{-2} (s.t.p.) $\times 10^7$	Analysis (mol %) H_2	N_2	CO	CO_2	H_2O	O_2	Note
1	1	Nil	HO	0.02	95						a
2	4	Nil	PO	0.03							b
3	1	Nil	HO	40.0	99.9						
4	1	Nil	HO	25.1	99.9						
5	1	Nil	PO	21.8	99.9						
6	1	Nil	HO	3.0	99						c
7	1	1200	PO	1.3	37	12	12	39			
8	1	1200	PO	0.1		25		45	25	5	
9	1	1300	PO	0.3	10	18		61			d
10	1	1300	PO	1.0	28	23	35	14			
11	2	Nil	PO	20.1	99.9						
12	2	1300	PO	0.4	29	29		40	2		
13	5	Nil	PO	> 14.2	< 12			< 10	> 78		
14	6	Nil	PO	0.6	29	19	19	33			
15	3	Nil	PO	0.3	25	13	13	47			e

*Glasses 1, 2, and 3 were standard grade fused quartz materials; glass 4 was a chemically resistant borosilicate glass; glass 5 was optical grade, high OH content fused quartz; glass 6 was an optical grade, low OH content fused quartz.

†Pretreatment refers to a heat treatment in air prior to fabrication of the ampoule. All ampoules were degassed *in vacuo* to at least 600 K.

‡HO indicates H_2–O_2 flame; PO indicates propane–O_2 flame.

a. Plus traces CO_2 and O_2. Ampoule held at room temperature, not heated to 1300 K.
b. Only traces of nitrogen and hydrocarbons smaller than background. Ampoule heated to 700 K only.
c. Degassed at 1200 K for 2 h instead of 600 K for 1 h.
d. Plus 10% SO_2, 1% H_2S.
e. Plus 2% CH_4.

showing that appreciable amounts of gas were not evolved by a chemically resistant borosilicate glass (glass 4) at 700 K nor by standard grade fused quartz at room temperature. Experiments 3 to 5 illustrate that the gas evolved at 1300 K from one standard grade fused quartz was essentially pure hydrogen and that a variation in amount by as much as a factor of two was observed. The effect of changing the fabrication flame from H_2–O_2 to propane–O_2 was negligible. The "propane" used did contain a few per cent of hydrogen and hydrocarbons other than propane. Experiment 6 shows that increasing the vacuum degassing temperature from 600 to 1200 K (and the degassing time to 3 h) did decrease significantly the hydrogen evolved. Experiments 7 to 10 illustrate that pretreating the glass at 1200 or 1300 K for 3 to 6 days in air prior to forming the ampoule was more effective, reducing the hydrogen evolved by about a factor of 40. These results encompass the variation in pressure and composition which was observed. Pretreatment at 1300 K was not superior to pretreatment at 1200 K. More prolonged pretreatment at either temperature had no apparent effect on the amount of hydrogen subsequently evolved. Occasionally, after pretreatment at 1200 K, no hydrogen was evolved from a sample (e.g. experiment 8) but this phenomenon was not reproducible. Experiments 11 and 12 show that glass 2, a standard grade fused quartz from another source, behaved similarly to glass 1. Glass 5, a high purity, high OH group concentration fused quartz, produced large amounts of water and only moderate amounts of hydrogen (experiment 13). Rapid adsorption of the water on the inlet walls and reaction of the water with the source filament (to produce CO_2), caused these results to be inaccurate. Without pretreatment, glasses 3 and 6 released quantities of gas similar to those released by 1 and 2 after pretreatment. Glass 3 was a standard grade material as were 1 and 2, whereas 6 was an optical grade, low OH group concentration glass.

4. Discussion

Two of the three standard grade fused quartz materials which were studied here, released hydrogen at high temperatures. Hydrogen evolution can be significant at temperatures as low as 1000 K. The gases measured here were those which evolved irreversibly *in vacuo* during the cycle room temperature – 1300 K-air quench to room temperature. Thus the total amount transferred to some gettering material in an ampoule could exceed the amounts measured in this work. For example, let us consider the preparation and two annealings of a 0.01 mol sample in such ampoules at 1300 K. Assuming efficient hydrogen gettering by the sample, an ampoule surface area of 25 cm^2 and an evolution rate of 2.5×10^{-6} litre-cm^{-2} (s.t.p.), the hydrogen contamination would be 1500 ppm or greater. This is illustrated by some results from this laboratory [5]. Lanthanum and its compounds appear to be more efficient getters of most gases than Erbium and its compounds. LaAs annealed in fused quartz ampoules (glass 1) exhibited a hydrogen level of 6000 ppm compared to 500 ppm in the starting materials. ErAs, similarly annealed, exhibited no such increase.

For static pressure measurements in a closed apparatus made of fused quartz, hydrogen pressures up to 50 torr at 1300 K may be observed if the material under study does not getter hydrogen. In this laboratory a room temperature pressure of up to 20 torr of HBr was observed in a fused quartz bourdon gauge apparatus after the system Mo/As/Br was cycled to 1300 K [6].

As shown above, pretreatment at 1200 to 1300 K of the fused quartz prior to fabrication of ampoules or other apparatus together with degassing at 600 K reduces the hydrogen evolved by about a factor of 40. Increasing the degassing temperature to 1200 K from 600 K is also reasonably effective, but at least several hours are required, and if the sample to be processed includes volatile components, degassing prior to loading would be required. This is a less convenient procedure.

It is evident that the use of glass 3, a standard grade fused quartz material or of the low OH group concentration optical grade (glass 6) without pretreatment would be equally effective in reducing hydrogen contamination. However, glass 6 is several times as costly as glasses 1, 2 and 3. As for glass 3, our experience with it is not extensive and its apparent superiority relative to other standard grade glasses may be a batch effect. It is equally possible that it was made in a furnace having a lower partial pressure of hydrogen or that it has been already heat treated by the manufacturer. Nevertheless we would recommend that standard grade materials from any source be subjected to the simple heating process described here prior to being used for materials handling or encapsulation at temperatures above 1000 K.

A mechanism both of hydrogen uptake by fused quartz and of its subsequent evolution is well known. Hydrogen can dissolve in the glass both as hydrogen molecules and as a constituent of hydroxyl groups. Its presence as molecular hydrogen in holes or interstices in the fused quartz has been demonstrated by the proportionality between the solubility and the partial pressure of hydrogen ([7] and references cited therein). Three types of OH group sites exist in fused quartz [8, 9], two of which can be removed or added at temperatures ≥ 800 K (metastable OH) and the third of which is not removable by vacuum degassing at 1300 K (permanent OH). Equilibria between both hydrogen and water vapours and at least the metastable types of OH groups has been demonstrated [10, 11]. In addition, hydrogen can be incorporated in the bubbles in the glass both as molecular hydrogen and as a component of water. Finally, hydrogen is known to readily diffuse through fused quartz at high temperatures [12]. These mechanisms together with the known presence of hydrogen during the fusion of standard grade fused quartz account for the inclusion of hydrogen in this material. The subsequent hydrogen evolution when this material is heated could occur both by desorption of molecular hydrogen and from metastable OH groups. In addition the effectiveness of the pretreatment procedure used here is consistent with these mechanisms. These mechanisms would lead one to expect negligible hydrogen evolution from glass 6 without pretreatment since it was made by vacuum fusion. Indeed, the traces of hydrogen which were evolved from this glass may well have been introduced into the glass during the fabrication of the test ampoule.

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