

Rupture-Disk Ampoule for Anhydrous Addition of Hydrogen Fluoride*

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The rapid increase in vapor pressure of liquid HF with temperature has been used in a rupture-disk-ampoule technique for mixing HF with materials under anhydrous conditions. At room temperature where HF has a vp near 1.4 atm, the disk with a rupture limit near 10 atm confines the acid. At higher temperatures, 100 and 150 °C, where the internal pressure of HF in the ampoule is 10 and 30 atm, respectively, the disk is ruptured and the acid is released. The construction of the ampoule from platinum and re-useable platinum-iridium parts; the details of the filling, sealing and weighing; and its use for anhydrous addition of HF to other materials in a closed vessel are described.

Key Words: Anhydrous filling, anhydrous mixing, ampoule, capsule, hydrogen fluoride, metal, rupture-disk.

1. Introduction

Glass ampoules with break-tips or thin walls have long been used for the two-fold purpose: one, sealing a volatile substance under its own vapor pressure for weighing, storage, protection of its purity, etc.; and two, providing for the transfer of the substance in the absence of air or moisture to other vessels and to other materials by breaking the tip or thin wall of the ampoule under controlled conditions. A metal, rupture-disk ampoule of platinum and platinum-iridium parts was designed to extend this technique to hydrogen fluoride, whereby: one, liquid HF is confined in the ampoule under its own vapor pressure by sealing the inlet tube of the ampoule; and two, HF is subsequently transferred to other vessels and to other materials under anhydrous conditions by rupturing the disk of the ampoule. Whereas breakage of the tip or thin wall of the glass ampoule is effected by the mechanical impact from a magnetic hammer or fused wire, the marked increase in the vapor pressure of liquid HF with temperature is used to rupture the disk of the metal ampoule. A disk of 0.025 mm platinum foil was selected, because disks of this thickness were found to rupture under a pressure near 10 atm in experiments in which nitrogen gas pressures from a cylinder were applied. This disk safely confines HF in the

sealed ampoule at 25 °C where liquid HF has a vapor pressure of about 1.4 atm. Rupture of the disk for anhydrous addition of HF to other materials is effected by raising the temperature which causes the internal pressure of HF in the sealed ampoule to increase to a value exceeding the rupture limit of the disk; at 100 and 150 °C, liquid HF has a vapor pressure of 10 and 30 atm, respectively.

2. Construction

Whereas other types of designs of rupture-disk ampoules based on this principle may be used, the cross-sectional drawing of the ampoule, shown in figure 1, was designed to fit inside a Morey pressure bomb. The ampoule is composed of four parts: a platinum inlet tube, A; a platinum-iridium shell, B; a platinum-iridium protective ring, C; and a rupture-disk of platinum foil, D. The ring C is not gold soldered to the shell and serves only as a protective guard for the thin platinum disk, D. The shell B is reused to form a new ampoule by gold soldering a new section of platinum tubing, A, at 4 and a new disk, D,² at 5 as described in the legend to figure 1.

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²Note: In the sealing of the platinum disk, D, to the shell B at position 5, the protective ring C should not be on the shell portion because of possible alloying through the thin foil D to both parts B and C. The reason for this precaution is as follows: the gold soldering can form with the thin platinum foil an alloy of 90 percent Pt and 10 percent Au which has a melting range of 2950–3125 °F and therefore cannot be unsoldered by heating from the Pt-Ir alloy (parts B and C) which have a melting point of 3290 °F. In the case of unsoldering the platinum tube A of 0.025 mm thickness no difficulty was experienced and the unsoldering behaved as expected from the melting points of Au (1945 °F), Pt (3200 °F) and the alloy of 90 percent Pt-10 percent Ir (3290 °F).

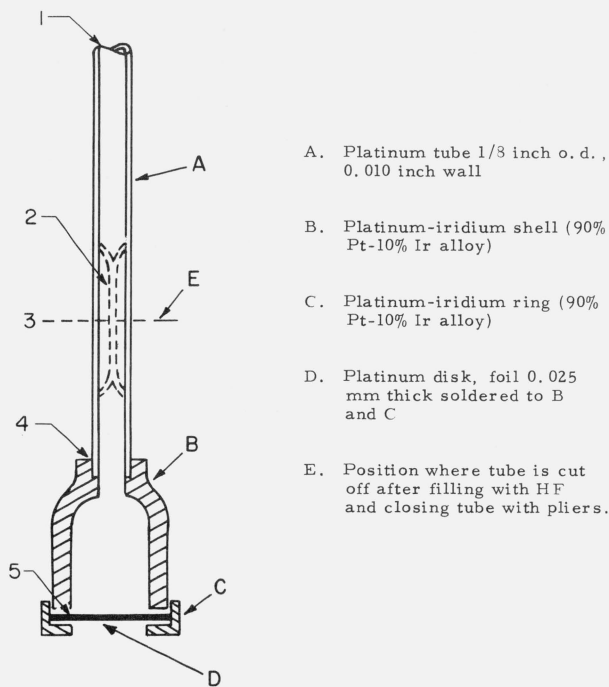


FIGURE 1. Rupture-disk ampoule.

3. Operation

For filling, the ampoule is attached at its position 1, figure 1, through a union fitting of Monel to a Monel manifold as shown in figure 2. This manifold is joined on one end to a cylinder of HF gas and on the other end to a high-vacuum system that contains a nickel-Monel trap. Before filling, the ampoule is first evacuated in this manifold to 10^{-6} mm Hg, tested for leaks with a helium-leak detector, filled with dry air to atmospheric pressure, disjoined from the manifold at the union coupling and weighed. After filling and sealing, the filled ampoule and inlet tube containing the attached union coupling are weighed. From this and the previous weighing, the amount of HF sealed in the ampoule is determined.

The sequence of operations that is usually performed in glass systems for sealing a volatile substance under its own vapor pressure in a glass break-off-tip ampoule was applied to the metal system of Monel and nickel parts which was used to seal HF under its own vapor pressure in a rupture-disk ampoule of platinum and platinum-iridium parts. These metals were selected because they offer good chemical resistance to HF whereas glass is attacked. Hydrogen fluoride lended itself well to these operations because of its following properties: boiling point near 19.4°C ; fp near -83°C where its vapor pressure is about 5mm Hg; and a vapor pressure at the temperature (-196°C) of a liquid-nitrogen bath near 10^{-6} mm Hg. By the same techniques used with glass systems, HF gas was transferred from a cylinder through the evacuated

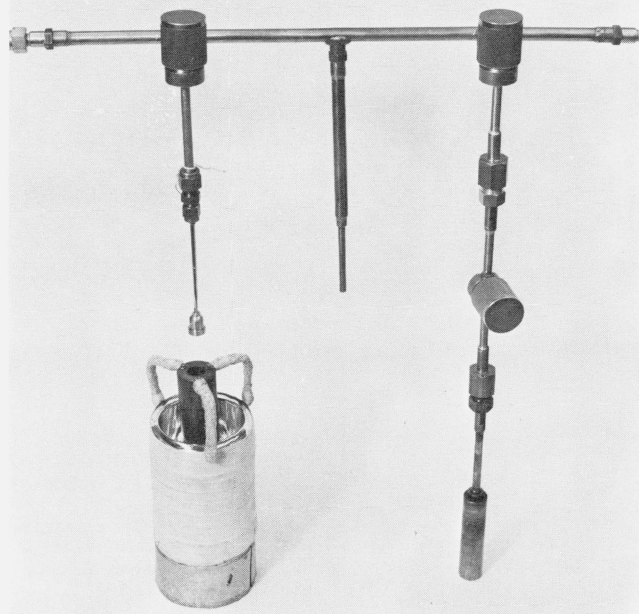


FIGURE 2. Manifold and coolant device used in filling and sealing hydrogen fluoride in an ampoule under its own vapor pressure.

manifold of Monel, condensed in a Monel-nickel trap, alternately frozen and melted in a vacuum to remove dissolved gases, transferred under its own vapor pressure to the rupture-disk ampoule, and then cooled in the ampoule by refrigeration in a liquid-nitrogen bath before sealing the HF in the ampoule under its own vapor pressure. Since most of these operations do not differ from the conventional practice with glass systems only the final cooling and sealing, which is different, will be described.

For the cooling, the ampoule is placed in the cavity of a solid copper rod that is immersed in a liquid-nitrogen bath. This rod is shown in figure 2 in an up-raised position for photographing. A contact medium, such as CCl_4 , that was added as a liquid and cooled as a solid to -196°C , was used to fill the space between the cavity and the ampoule for the purpose of improving the heat transfer between the ampoule, rod, and bath. After cooling the filled ampoule in this manner, the inlet tube A was compressed by pliers with parallel jaws as shown at 2 in figure 1. This compressed section had been previously annealed to soften the platinum, gold coated on its inner surface, and partially compressed so that a small coil of gold wire fitted just above position 2 in figure 1. After the compression with the pliers, this gold wire is heated to fusion as a final precaution in the sealing. The ampoule after this sealing is allowed to warm to room temperature, tested through the manifold system for leaks, and then disconnected at the union fitting and weighed. After weighing, the ampoule is disjoined from the inlet tube by cutting at position 3 as shown in figure 1.

4. Results

In a filling of this ampoule with a 0.429 g amount of HF, the reweighing of the filled ampoule after a week-end was constant to 1 mg. This weight was also checked to within 1 mg from the reweighing of the empty ampoule after an experiment in which the ampoule was placed in a bomb and heated to about 125 °C to release the HF to the cavity of the closed bomb.

5. Conclusion

This technique for the anhydrous addition of a weighed amount of HF in a rupture-disk ampoule was perfected for use in the development of a new hydrofluorothermal process whereby crystal growth of BeF₂ in a platinum-lined bomb under HF pressure was to be performed by a method analogous to that used in the hydrothermal growth of quartz from SiO₂. In the hydrofluorothermal method, BeF₂ was to replace SiO₂, HF was to replace H₂O, and NH₄F was to be substituted for NaOH as the flux material. Whereas in the hydrothermal process water is a component and is therefore no problem, the mixing of HF, BeF₂ and NH₄F in the bomb under anhydrous conditions was a major problem solved by the rupture-disk ampoule technique.

Although the ampoule discussed was specifically designed for use in the above process, this technique is described because of its general utility in other applications where a weighed amount of HF is to be mixed with other materials or added to vessels under anhydrous conditions. The filled and sealed ampoule allows HF to be added at room temperature to vessels under anhydrous conditions along with nonvolatile solids; and after closure of the vessel to be mixed with the contents of the closed vessel.

In cases where heating the HF-filled and sealed ampoule is not desirable, the disk may be punctured by mechanical impact by techniques such as fusing a wire to release a weight for puncturing the disk.

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