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The UF_6 Manual

Good Handling Practices for Uranium Hexafluoride

USEC-651, Revision 8
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This manual may be purchased from USEC Inc. for $49.95 plus shipping.

FOREWORD

On July 1, 1993, the United States Enrichment Corporation (USEC) assumed responsibility for operating the gaseous diffusion plants at Paducah, Kentucky, and Portsmouth, Ohio.

Beginning in 1966, guidelines for packaging, measuring and transferring uranium hexafluoride (UF_6) have been issued periodically by the U.S. Department of Energy (DOE) in its ORO-651 series. USEC has taken charge of updating and maintaining this information.

History of the Document

In 1957, K-1323, *A Brief Guide to Handling UF_6* was published. This was superseded in 1966 by the first issue of ORO-651. ORO-651 was reissued in 1967 to make editorial changes and to provide minor revisions in procedural information. In 1968 and 1972, Revisions 2 and 3, respectively, were published to reflect current conditions and information. Revision 4, issued in 1977, included updates for information on cylinders, valves and methods of use. In 1987, Revision 5 added material dealing with pigtails, overfilling cylinders, handling precautions, cylinder heel reduction procedures and definitions. Weighing standards previously presented in ORO-671, Volume 1, *Procedures for Handling and Analysis of UF_6* were also included; thus Revision 5 superseded ORO-671-1. Revision 6 of ORO-651, which was issued in 1991, added sections on quality assurance and storage of UF_6 as well as an expanded discussion of UF_6 physical and chemical properties. Revision 7, which was issued in 1995, was the first document in the series issued by USEC. The seventh revision was issued as USEC-651 to continue the series numbering.

Revision 8

This edition, titled *The UF_6 Manual: Good Handling Practices for Uranium Hexafluoride,* USEC-651, is the eighth revision in a continuing effort to keep the information current with developing technologies and agreements for the supply of enriched uranium. Revision 8 of USEC-651 updates information in previous revisions of the document. The guidelines set forth in this document will normally apply in all transactions involving receipt or shipment of UF_6 by USEC unless stipulated otherwise by contracts or agreements with USEC. *The UF_6 Manual* is made available to the industry as a public service of USEC. It is not a rule or regulation of the U.S. government under the Administrative Procedure Act (APA) or any other provision of U.S. law, nor are the approvals by USEC described herein a license for purposes of the APA or other law. The requirements for how the USEC plants operate are found in USEC's Certificate of Compliance issued by the Nuclear Regulatory Commission (NRC). USEC's Certificate may be changed from time to time. In the event of a conflict between this guidance manual and the Certificate, the latter document shall govern.

Any questions or requests for additional information on the subject matter covered herein should be directed to USEC Inc., 6903 Rockledge Drive, Bethesda, Maryland, 20817, Attention: Vice President of Production.

UF_6 PHYSICAL AND CHEMICAL PROPERTIES

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4.1 General

Uranium hexafluoride is a compound of hexavalent uranium and fluorine. It is the process gas used by gaseous diffusion plants to increase the concentration of the fissionable isotope uranium-235 in the mixture of uranium-238, uranium-235 and uranium-234 found in naturally occurring uranium ore. UF_6 is used for two reasons. First, it can conveniently be used as a gas for processing, as a liquid for feeding and withdrawing and as a solid for storage. Each of these states is achievable at relatively low temperatures and pressures. Second, because fluorine has only one natural isotope, all the isotopic separative capacity of the diffusion plant is used to enrich the concentration of the lighter uranium isotopes.

4.2 Chemical Characteristics

In the solid state, UF_6 is a nearly white, dense crystalline solid. The appearance of the solid is a function of whether it was formed by freezing from the liquid phase or desubliming from the vapor phase. In the first case, the solid particles will be irregularly shaped grains somewhat like rock salt, and in the second case, the solid will be a formless mass. The liquid is colorless and, even though it is very heavy, has a low viscosity so it flows freely and completely wets the surface of its container. The liquid phase is not stable at atmospheric pressure. The gas is colorless.

Uranium hexafluoride does not react with oxygen, nitrogen, carbon dioxide or dry air; however, each of these gases is soluble in the UF_6 liquid phase and very much less soluble in the solid phase. Gaseous UF_6 does react rapidly with water vapor as does the exposed surface of solid UF_6. Because of this, UF_6 is always handled in leak-tight containers and processing equipment to prevent it from reacting with water vapor in the air. The reaction of gaseous UF_6 with water vapor at elevated temperatures is shown in Equation 1.

Equation 1

$$\underset{\text{(gas)}}{UF_6} + \underset{\text{(vapor)}}{2H_2O} \rightarrow \underset{\text{(solid)}}{UO_2F_2} + \underset{\text{(gas)}}{4HF} + \text{heat}$$

At room temperature, depending upon the relative humidity of the air, the products of this reaction are UO_2F_2 hydrates and HF-H_2O fog, which are seen as a white cloud. A typical reaction with excess water is given in Equation 2.

Equation 2

$$\underset{\text{(gas)}}{UF_6} + \underset{\text{(vapor)}}{(2+4x)H_2O} \rightarrow \underset{\text{(solid)}}{UO_2F_2 \cdot 2H_2O} + \underset{\text{(fog)}}{4HF \cdot xH_2O} + \text{heat}$$

If, because of extremely low humidity, the HF-H_2O fog is not formed, the finely divided UO_2F_2 causes only a faint haze. The UO_2F_2 is a water soluble, yellow solid whose exact coloring depends on the degree of hydration as well as the particle size.

The heat release for this reaction, as written in Equation 1, is 124 BTUs per pound of UF_6 gas reacted. The heat release is much larger if the UO_2F_2 is hydrated and HF-H_2O fog is formed. Thus, the heat release for Equation 2 is 1057 BTUs per pound of UF_6 vapor, due mostly to the condensation of water vapor as it is incorporated into the UO_2F_2 hydrate and the HF-H_2O fog, and to the interaction of the HF and the water. For solid UF_6 and liquid water to form a solution, as shown in Equation 3, the heat release will be 258 BTUs per pound of solid UF_6 reacted.

Equation 3

$$UF_6 + 1602H_2O \rightarrow UO_2F_2(aq,4HF/1600H_2O) + heat$$

(solid) (liquid) (liquid)

Most of the additional heat released by the reaction in Equation 3, over that of the reaction in Equation 1, is from the interaction of HF and water; however, the rate of heat release is usually considerably slower because the complex uranium oxyfluoride layer formed on the surface of the solid UF_6 constitutes a diffusion barrier that limits the access of water to the UF_6 surface. This also explains the slow hydrolysis rate of solid UF_6 by water vapor, while the reaction in the gas phase is almost instantaneous.

When there is a release of UF_6 as a gas to the atmosphere, reactions similar to that shown in Equation 2 normally occur, and the visible white cloud rises rapidly because of the heat generated by the reaction.

Uranium hexafluoride reacts with most metals to form a fluoride of the metal and a poorly volatile or nonvolatile lower-valence uranium fluoride. Nickel and nickel-plated steel, Monel, copper and some aluminum alloys are generally used for processing equipment. Mild steel is corroded by UF_6 and the resulting film greatly reduces, but does not prevent, further attack. Steel is used for shipping and storage cylinders because the small amount of corrosion that occurs does not warrant the cost of more expensive metals.

Great care must be taken to avoid introducing hydrocarbon oil into processing equipment or cylinders.

Uranium hexafluoride reacts rapidly with hydrocarbons. If the UF_6 is in the gas phase, the reaction forms a black residue of uranium-carbon compounds. In the liquid phase, the reaction proceeds at an accelerated rate and has been known to cause explosions in cylinders. Great care must be taken to avoid introducing hydrocarbon oil into processing equipment or cylinders.

Uranium hexafluoride is a chemically stable compound. However, in a field of intense alpha radiation, it slowly decomposes to solid UF_5 and fluorine gas.

4.3 Physical Properties

4.3.1 Phase Diagram

Safe handling of UF_6 requires a detailed knowledge of its physical characteristics. Because UF_6 is always processed in leak-tight piping, equipment and containers, it is not visible to the operator. The operator must follow its presence by observing changes in pressures or weights. Such changes are conveniently illustrated by means of a phase diagram that shows the physical state (*i.e.*, solid, liquid, or gas) of UF_6 as a function of its pressure and temperature. It should be noted that these data are for UF_6 alone, as a single-component system. If air, nitrogen, HF or other gases are present, the total pressure condition for a given temperature will be higher, *i.e.*, the sum of the partial pressures of the system components.

Figure 3 is the phase diagram covering the range of conditions usually encountered in working with UF_6. It shows the correlation of pressure and temperature with the physical state of the UF_6. The triple point occurs at 22 psia and 147.3°F. These are the only conditions at which all three states – solid, liquid and gas – can exist together in equilibrium. If the temperature or pressure is greater than at the triple point, there will be only gas or liquid. If the temperature or pressure is lower, there will be only solid or gas. For instance, at atmospheric pressure, 14.7 psia, there can only be gas or solid, regardless of the temperature. At 100°F, for example, the pressure of gas over solid is 5 psia. This is a typical condition in a UF_6 cylinder in storage.