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The Physical and Chemical Properties of Uranium Hexafluoride*

by E. J. Barber

Corporate Fellow, Martin Marietta Energy Systems, Inc.,
Oak Ridge, Tennessee, USA

ABSTRACT

This paper describes what uranium hexafluoride (UF_6) is, gives some of its pertinent physical properties, illustrates significant reactions between UF_6 and other substances, touches on its toxic properties, and states some of the "do's" and "don't's" of UF_6 handling. At room temperature, UF_6 is a colorless, high molecular weight, subliming solid with a significant vapor pressure. The triple point is at 64.02°C (337.17 K) and 1.497 atm (0.1517 MPa). Because the pressure of liquid UF_6 is always above 1 atm, the behavior of a ruptured cylinder containing liquid UF_6 will be similar to that of a superheated hot water heater, but somewhat less violent. In both the solid and liquid states, UF_6 is highly expanded; that is, the number of molecules per unit volume is smaller than for most other substances. The change in density between the liquid and solid states is about one-third, an abnormally large increase.

The value of $(\partial P/\partial T)_V$ for liquid UF_6 is 4.8 atm/°C (0.485 MPa/K) at 150°C (423.2 K). The corresponding value for solid UF_6 is 30.2 atm/°C (3.06 MPa/K) at –40°F (233.2 K). These values help in understanding the rupture of overfilled cylinders and the bulging of cold traps. Values for other physical properties which aid in understanding the nature of the UF_6 molecule are also given.

The key to much UF_6 chemistry is the great stability of the uranyl ion (UO_2^{++}), which permits the reaction with water, oxides, hydroxides, and salts containing oxygen-bearing anions without having to liberate molecular O_2, a high potential barrier process. The UF_6 is a relatively mild fluorinating agent but is reactive toward metals and most organic materials. Liquid UF_6 reacts with hydrocarbons with explosive violence. Silicones are destroyed by UF_6. The UF_6 is toxic per se and is also toxic because of the HF generated by hydrolysis. The biological half-life is short because the uranyl ion is rapidly eliminated from the body by the kidneys. In closing, the implications of the properties of UF_6 are summarized in terms of a few rules for handling.

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NOMENCLATURE

$(\partial P/\partial T)_V$	Rate of pressure rise per unit increase in temperature at constant liquid volume (atm/K)
P	pressure due to UF_6 acting on the cylinder walls and the pressure exerted by or upon the liquid or solid UF_6 (atm or other consistent unit)
T	temperature (K)
(dT_m/dP)	change in the temperature of fusion (melting) per unit change in pressure on the solid (K/atm)
T_m	temperature of fusion (K)
ΔV	molar volume change on melting (L)
ΔH_f	molar enthalpy of fusion (L-atm/mol)
$\rho(s)$	density of the solid (g/mL or kg/L) at temperature t
$\rho(l)$	density of the liquid (g/mL or kg/L) at temperature t
t	temperature (°C)
t_c	critical temperature (°C)
α	volume coefficient of expansion defined by the relation $\alpha = (1/V)(\partial V/\partial T)_P$ (reciprocal degrees)
β	coefficient of compressibility defined by the relation $\beta = -(1/V)(\partial V/\partial P)_T$ (atm^{-1})
$(\partial P/\partial T)_{V(s)}$	rate of pressure increase per unit temperature increase in restrained solid UF_6 (atm/K)
P_{max}	maximum pressure that could be developed in restrained solid UF_6 trapped at a given desublimation temperature and heated to another temperature differing by ΔT (K)
C_p	molar heat capacity at constant pressure (cal/mol-K), the phase to which it applies will be indicated in parentheses following [e.g., $C_p(g)$ for the gas phase]

INTRODUCTION

This paper is intended to provide a description of what UF_6 is, some of its pertinent physical properties, illustrations of the reactions between UF_6 and other substances, some concepts about UF_6 reactions important to processing, and some "do's" and "don't's" of UF_6 handling and transporting.

At room temperature, UF_6 is a colorless, high molecular weight, nonpolar, subliming solid with significant, but less than atmospheric, vapor pressure. This statement immediately indicates that one will not be handed a bag containing UF_6 or a bottle of liquid UF_6 but that one will probably receive the UF_6 in a metal tube sealed by a valve or valves. The contents of the tube will not be subject to visual inspection and therefore must be determined by analysis.

PHYSICAL PROPERTIES

Phase Diagram[1]

The phase diagram for pure UF_6 is shown in Figure 1 in which the logarithm of the vapor pressure is given as a function of the temperature. Only vapor exists in the region to the right and below the continuous curve. The liquid exists to the right of the dotted line and above the continuous line but to the left of the critical-point temperature, above which temperature the liquid and vapor are indistinguishable. The liquid range is relatively long, and the critical pressure is relatively large, about 45.5 atm (4.61 MPa), for a material of this class. As will be emphasized by others, UF_6 storage cylinders are not designed to withstand such pressures. The area to the left of the dashed and continuous curves represents conditions under which the solid UF_6 exists.

Note that the sublimation temperature is below the triple point. This has implications for processing because the pressure must be above 1.5 atm (0.152 MPa) and the temperature above 64°C (337 K) for UF_6 to be handled as a liquid. Thus, any process using liquid UF_6 will be subject to leakage of the UF_6 to the atmosphere through any holes. Also, because the pressure of liquid UF_6 is always above 1 atm, the behavior of a ruptured cylinder may be similar to that of a superheated hot water heater, although somewhat less violent. Transfers below 1.5 atm or below 64°C involve moving vapor that is produced by sublimation and removed by desublimation in a cooled trap.

Density of UF_6

The UF_6 is a relatively expanded liquid and solid; that is, the number of molecules per unit volume of liquid and solid are relatively fewer than in most other materials. Still the densities are quite large, as seen from Figure 2 in which the densities of solid and liquid UF_6 are shown as functions of temperature. Equations expressing the density of the solid and liquid as a function of temperature are given below. Equation 1 comes from refs. 2 and 3, Equation 2 from ref. 4, and Equation 2a from ref. 5.

$$\rho(s) = 5.194 - 0.005168\,t, \quad g/mL, \qquad (1)$$

$$\rho(l) = 1.670 + 0.15203\,(230.2 - t)^{0.5}, \quad g/mL, \qquad (2)$$

or

$$\rho(l) = 2.0843 - 0.0031\,t + 0.3710\,(230.2 - t)^{0.3045}, \quad g/mL, \qquad (2a)$$

Equation 2 is probably more accurate near the triple point, and Equation 2a is more accurate near the critical point.

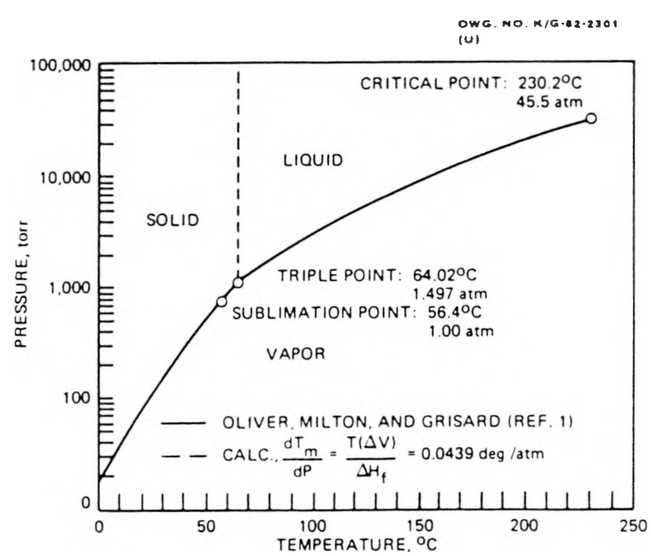

Figure 1. UF_6 phase diagram.

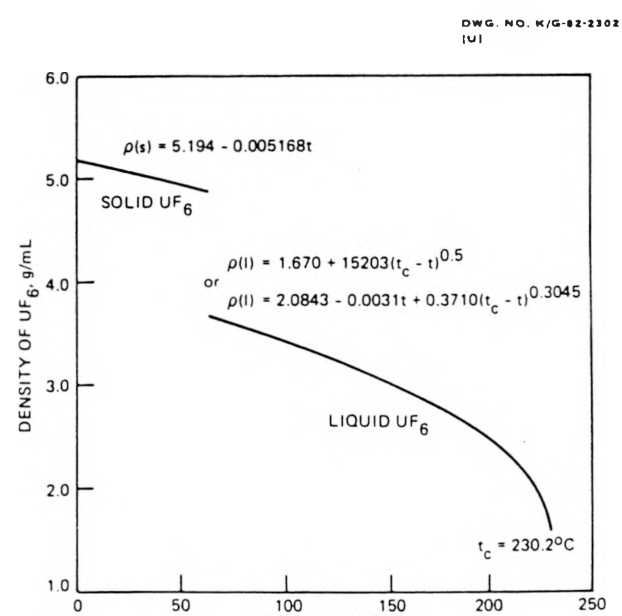

Figure 2. Density of UF_6.

Two factors influencing handling should be stressed. First, the coefficients of expansion and compressibility are noted to be relatively large for both the solid and the liquid. Rapid heating of desublimed solid may lead to trap bulging with metals and to breakage with glass containers, whether or not the trap is overfilled.[3] Second, for handling liquid UF_6, sufficient freeboard (ullage) must be maintained to provide for liquid expansion for the temperature range over which the liquid is to be heated.[4] Particular attention must be paid to the fill limits of containers when the UF_6 is to be desublimed as solid and is to be liquified for removal. The volume of the liquid produced on melting is about four-thirds of the volume of the solid.

The consequences of heating a cylinder once it has been completely filled with liquid UF_6 may be deduced from the data in Figure 3, which shows the rate of increase of the pressure of liquid UF_6 with temperature at constant volume as a function of the temperature at which the cylinder becomes filled.[4] These values may be computed using Equation 3.

$$(\partial P/\partial T)v = 11.42331 - 5.96051 \times 10^{-2} t + 1.02420 \times 10^{-4} t^2, \text{ atm/°C}, \quad (3)$$

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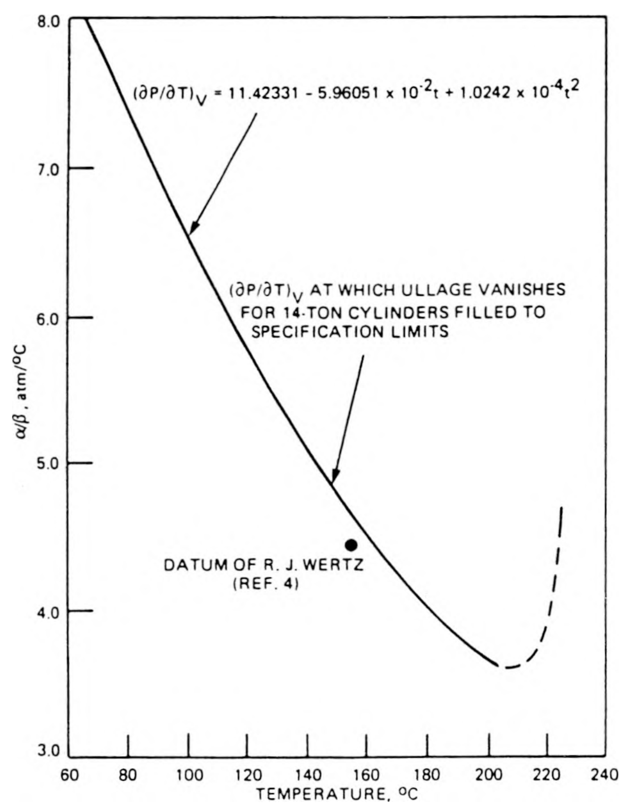

Figure 3. Rate of change of pressure with temperature at constant volume for filled UF_6 cylinders assuming an Eyring liquid.

A similar equation may be derived for use in estimating pressure in the restrained solid.[3] The value of $(\partial P/\partial T)v(s)$ at a given desublimation temperature is given by

$$(\partial P/\partial T)v(s) = 2.6137 [\rho(s) - 2.353]^{2.06025} + 3.616, \text{ atm/°C}, \quad (4)$$

so that

$$P_{max} = (\partial P/\partial T)v(s) \times \Delta T. \quad (5)$$

The maximum pressure that could be developed by UF_6 trapped at −100°F (200 K) and heated near the melting point is 69,000 psi (476 MPa).

Other Physical Properties of UF_6

A number of properties are listed in Table 1 to give a better feel for the nature of the UF_6 molecule. Note the small value for the heat of vaporization, which means that masswise, condensation and sublimation of material may occur a lot faster than one would expect for more familiar materials with a given heat flux. The heat capacity of the vapor is large with respect to those of normal atmospheric gases, which means, for example, that UF_6 is a much more effective quenching agent than nitrogen for exothermic gaseous reactions. The

Table 1. Other Physical Properties of UF_6

Heat of sublimation (at 64.05°C), kcal/mol	11.38
Heat of fusion (at 64.05°C), kcal/mol	4.56
Heat of vaporization (at 64.05°C), kcal/mol	6.86
Molar heat capacity of solid (at 25°C, Cp), cal/mol-°C	39.86
Molar heat capacity of liquid (at 72°C, Cp), cal/mol-°C	45.84
Molar heat capacity of vapor (at 25°C, Cp), cal/mol-°C	30.93
Cp/Cv (at 60°C)	1.067
Self-diffusion coefficient, vapor (at 30°C, 10 torr), cm^2/s	1.26
Self-diffusion coefficient, liquid (at 69.5°C), cm^2/s	1.90×10^{-5}
Viscosity of vapor (at 25°C), micropoise	176
Viscosity of liquid (at 70°C), centipoise	0.910
Thermal conductivity of vapor (at 50°C), cal/cm-sec-°C	1.76×10^{-4}
Thermal conductivity of liquid (at 72°C), cal/cm-sec-°C	3.83×10^{-4}
Thermal conductivity of solid (at 50°C), cal/cm-sec-°C	1.13×10^{-4}

combination of low surface tension, low viscosity, and high density leads one to expect quite small droplets and thus streaming in distillation columns at very low throughputs with some resultant design problems, such as how to ensure uniform wetting and flow throughout a column. Attention is called to the apparent discrepancy in the value of the triple point given in Figure 1 and Table 1 of 0.03°C. The value of 64.02°C is obtained experimentally by boiling the UF_6 under a nitrogen atmosphere. The dissolved nitrogen in the liquid UF_6 depresses the triple point by 0.03°C; thus, the triple point under the orthobaric pressure is 64.05°C.

CHEMICAL PROPERTIES

Chemistry of UF_6 (ref. 6)

The chemistry of UF_6 is largely determined by its fluorination (or oxidation) potential and the ease with which the UF_6 molecule is hydrolyzed (the U-F bond is a strongly polar bond as compared with the S-F bond in SF_6, which does not hydrolyze at all). The UF_6 is a very stable vapor having a dissociation pressure of about 10^{-30} atm at 400 K in the presence of solid UF_5 (ref. 7). Thus, UF_6 is a relatively mild fluorinating agent as can be seen from its position in the series below, fluorine being the most powerful and SF_6 being inert at room temperature:

$$SF_6 < WF_6 < UF_6 < TcF_6 < NpF_6 < PtF_6 < PuF_6 < ClF_3 < F_2. \quad (6)$$

This does not mean that UF_6 does not attack metals vigorously. The UF_6 tends to be strongly chemisorbed on most materials, giving a high surface coverage and consequently good molecular contact and greatly increasing the opportunity for reaction.

Table 2 illustates the types of chemical reaction undergone by UF_6. The key to much UF_6 chemistry is the great stability of the UO_2^{++} ion, which permits reaction with water, oxides, hydroxides, and salts containing oxygen-bearing anions such as SO_4^{--}, NO_3^-, and CO_3^{--} without having to liberate molecular O_2, which is a high potential barrier process. Thus, UF_6 is rapidly hydrolyzed by water to UO_2F_2 or one of its solvates, depending on the quantity of water relative to the stoichiometric requirement. Metathesis reactions are illustrated by the reaction with NiO and $Ni(OH)_2$. The UF_6 may form adducts as illustrated by the reaction with the alkali metal fluoride, NaF, to form $NaUF_7$ and Na_2UF_8. The UF_6 is an oxidizing agent toward metals and is reduced to form solid products such as UF_5, U_2F_9, U_4F_{17} and UF_4. The UF_x product produced depends on the partial pressure of the UF_6, the metal attacked, and the temperature so that the stoichiometry of the reaction is not unique.

The problem of chemisorption has already been mentioned; it occurs with almost every material except for a few fluorocarbon materials like polytetrafluoroethylene (Teflon TFE) and copolymers of tetrafluoroethylene and hexafluoropropene (Teflon FEP).

Table 2. Chemical Properties of UF_6

- Is easily hydrolyzed as gas, liquid, or solid
  - $UF_6 + 2H_20 \rightarrow UO_2F_2(s) + 4HF(g)$
- Carries out metathesis reactions with oxides, hydroxides
  - $UF_6 + 2NiO \rightarrow UO_2F_2(s) + 2NiF_2(s)$
  - $UF_6 + Ni(OH)_2 \rightarrow UO_2F_2(s) + NiF_2(s) + 2HF(s)$
- Forms "addition" complexes
  - $UF_6 + 2NaF \leftrightarrow Na_2UF_8$
- Oxidizes metals and is itself reduced
  - $2UF_6 + Ni \rightarrow 2UF_5 + NiF_2$
  - Other reduction products include U_2F_9, U_4F_{17}, UF_4
- Is frequently chemisorbed
- Is unreactive toward H_2, N_2, O_2 at ambient temperature
- Reacts with many organic materials
  - Attack is most vigorous at the functional group (exceptions: ethers and tertiary amines)
  - Fully fluorinated materials are quite resistant at moderate temperatures
  - Condensed phase reactions can be vigorous
- Is soluble in materials with which it does not react
- Destroys silicones

In addition to the rare gases, a few other gases of significance, including N_2, O_2, and H_2, are unreactive with UF_6 at room temperature. Advantage has been taken of this in some separation processes.

Regarding reactivity with organic materials, when attack occurs, it most often starts on the functional groups. Only the tertiary amine, $C\text{-}N=(C)_2$, and the ether, C-O-C, bonds are as resistant to rupture on fluorination as the C-C bond. Organic materials are significantly less reactive with UF_6 vapor than with UF_6 liquid. Hydrocarbons react in a controllable fashion with UF_6 vapor but may react with explosive violence with liquid UF_6.

Fully fluorinated materials such as Teflon TFE, Teflon FEP, and polyhexafluoropropene oxide (Krytox) and similar materials are essentially resistant to fluorination at the temperatures normally employed for handling UF_6 as a liquid. It should be noted that UF_6 has a tendency to dissolve in these materials and others with which it is unreactive or only slowly reactive. In doing so, it obeys the normal principles governing the solubililty of one substance in another.[2,8] One special class of materials, the silicones, are recognized as exhibiting excellent resistance to oxidation in oxygenating atmospheres to relatively high temperatures; and they are not at all stable in UF_6, with which they react to form UO_2F_2 and substituted fluorosilanes.

Toxicity of UF_6 (ref. 9)

Elemental uranium is a highly toxic material on an acute basis. Uranium hexafluoride vapor is toxic per se, producing some kidney damage and hydrolyzing to produce HF, which is itself a regulated toxic substance. The threshold limit value (TLV), which is the allowable 8-hour exposure level for industrial workers, is 3 ppm for HF. This value of the TLV for HF translates into a TLV for UF_6 of 0.75 ppm (volume basis) based on the fact that one UF_6 molecule produces four molecules of HF as the essentially instantaneous hydrolysis in the atmosphere occurs. Fortunately, the UO_2^{++} ion has a short biological half-life, and any UO_2F_2 absorbed through the lungs or injested orally is rapidly eliminated from the body by kidney action, thus minimizing the damage.

HANDLING RULES : SOME DO's AND DON'T's WITH UF_6

A few rules for handling UF_6 can be based on the implications of the properties of the compound:

1. Handle UF_6 in a sealed system having vacuum capability to aid in transfers. Liquid transfers are possible in a system that can be operated above about 1.5 atm (0.152 MPa) and 64.05°C (337.20 K).

2. Keep UF_6 away from moisture; otherwise, it will be lost from the gas phase as UO_2F_2.

3. Don't breathe UF_6 or its reaction products. Get respiratory protection before handling heated containers; handle them preferably in a fume hood.

4. Leave at least 40% ullage in cold traps.

5. Don't hook UF_6 cylinders directly to vacuum pumps.

6. Remember that liquid UF_6 and organic materials, other than fluoroplastics, can react violently. (Do not heat cylinders known to contain UF_6 and liquid hydrocarbons.)

SUMMARY

In summary, be reminded that the properties of UF_6 determine how it must be handled and make direct observation impossible. To determine that the material in a container is UF_6, one must use other instruments in addition to a scale. Because of the very large volume expansion of UF_6 upon melting, diligence must be exercised in filling cylinders in which the UF_6 is partially solidified. A cylinder of liquified UF_6 with no ullage is potentially the equivalent of a superheated hot water heater, not just a hydraulically overpressurized cylinder. Finally, UF_6 can be handled safely by careful attention to the suggested precautions.

REFERENCES

1. G. D. Oliver, H. T. Milton and J. W. Grisard, "The Vapor Pressure and Critical Constants of UF_6," *J. Am. Chem. Soc.* **75**, 2827–9 (1953).

2. R. DeWitt, Uranium Hexafluoride: *A Survey of the Physico-Chemical Properties*, GAT-280, Goodyear Atomic Corporation, Portsmouth, Ohio, Aug. 12, 1960.

3. E. J. Barber, *Estimation of Pressures Developed by Restrained Solid Uranium Hexafluoride*, K/ET-307, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, Sept. 14, 1979.

4. E. J. Barber, *Relationship of Pressure to Temperature Rise in Overfilled Cylinders*, K/ET-194, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, May 18, 1979.

5. R. J. Wertz and W. D. Hedge, *Density of Liquid Uranium Hexafluoride*, K-1466, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, Feb. 1, 1965.

6. J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium. Part I: The Element, Its Binary and Related Compounds*, National Nuclear Energy Series, Division VIII, Vol. 5, McGraw-Hill Book Company, New York, 1951.

7. J. M. Leitnaker, *Thermodynamic Data for Uranium Fluorides*, K/PS-352, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, March 1983.

8. J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, Third Edition, American Chemical Society Monograph Series, Reinhold Publishing Corporation, New York, 1950.

9. N. I. Sax, *Dangerous Properties of Industrial Materials*, Sixth Edition, Van Nostrand Reinhold Company, New York, 1984, p. 2711.