### Notes

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## Xenon hexafluoride-uranium pentafluoride complexes\*

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XENON hexafluoride is known to form a number of addition compounds with the alkali fluorides. The compounds are of general formula MF .  $XeF_6$  (M = Cs or Rb) and 2 MF .  $XeF_6$  (M = Cs, Rb, K or Na) [1]. Xenon hexafluoride reacts with the pentafluorides of antimony[2], arsenic[3], tantalum[4], and vanadium[5] yielding compounds of the type  $mMF_5$ .  $nXeF_6$  where m and n are 2 or 1 depending on the conditions used and on the specific properties of the pentafluoride. Furthermore, xenon hexafluoride combines with the tetrafluorides of tin[6] and germanium[7], with boron trifluoride[3] presumably fluoride ion acceptors and with nitrosil-[5] and nitroxyl-[8] fluorides presumably fluoride ion donors like the alkali fluorides.

In the course of our attempts to prepare pure xenon tetrafluoride we tried to reduce xenon hexafluoride using uranium tetrafluoride as a reducing agent. When a high surface area uranium tetrafluoride was treated with excess of xenon hexafluoride at room temperature, uranium hexafluoride and xenon tetra- and hexafluoride were the only volatiles detected by i.r. spectroscopy after a few hours of reacting. The solid remaining, after the volatiles were removed, showed a composition corresponding to the general formula UF<sub>5</sub>. 1,75 XeF<sub>6</sub>. Upon prolonged pumping at room temperature this product decomposed yielding a compound of the composition UF<sub>5</sub>. XeF<sub>6</sub>. The same pale yellow compound was obtained also when uranium pentafluoride was treated with xenon hexafluoride and the volatiles were removed by extensive pumping off at room temperature. The compound UF<sub>5</sub>. XeF<sub>6</sub> is soluble in anhydrous hydrogen fluoride to form bluish green solutions from which it can be recrystalized unchanged. The magnetic susceptibility of the solid obeys the Curie-Weiss law within the temperature region 90–290°K. The effective magnetic moment of the compound is 1.57 B.M. with the Weiss constant  $\theta$  amounting – 55°K.

### EXPERIMENTAL

*Materials*. Uranium tetrafluoride with a surface area of approximately  $8 \text{ m}^2/\text{g}$  was prepared by the thermal decomposition of hydrazinium (1+) pentafluorouranate as described elsewhere[9]. Uranium pentafluoride was prepared by controlled fluorination of uranium tetrafluoride at 80°C with elemental fluorine[10]. Xenon hexafluoride was prepared by pressure synthesis from the elements and purified by repeated pumping off the volatiles at  $-80^{\circ}C[11, 12]$ .

*Apparatus*. Preparations were carried out in argon-arc welded nickel pressure or weighing vessels equipped with brass valves and using all nickel pressure or vacuum systems. Anhydrous hydrogen fluoride solutions were prepared and handled in all Kel-F system[13].

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**Preparation.** In a typical run about 5 m-mole of uranium tetrafluoride were weighed into a thinwalled nickel can and its contents were seasoned at room temperature by fluorine and subsequently by uranium hexafluoride vapour in order to remove the traces of water possibly present. After the system has been thoroughly pumped out, an excess of xenon hexafluoride was added and allowed to react at room temperature for several hours. I.R. spectra of the volatiles pumped off the reaction vessel show besides of xenon hexafluoride the presence of uranium hexafluoride and xenon tetrafluoride. The later compound seems to be the only product of xenon hexafluoride reduction whereas the oxidation of uranium tetrafluoride appears to be more complex. Material balance was carefully followed throughout the experiments, however, we could not find any obvious relation between the amount of uranium hexafluoride formed and the excess of xenon hexafluoride used over the stoichiometrical amount needed for the formation of  $UF_5 \cdot 2 XeF_6$ . Therefore, it was concluded that uranium hexafluoride might be formed as a product of some side reaction during the oxidation of uranium tetrafluoride.

In one case the weight of the reaction vessel was followed in the course of pumping off the volatiles. The curve obtained plotting total weight versus time of pumping presented in Fig. 1, shows that the solid product of the reaction  $UF_5$ .  $XeF_6$  does not have any appreciable vapour pressure. The change in slope of the curve corresponds to the composition  $UF_5$ .  $2XeF_6$ . The vapour pressure of this compound at room temperature is roughly estimated as less than 5 mm Hg.



Fig. 1. Dependence of the total weight of the sample of the time of pumping off in the course of  $UF_6$ . XeF<sub>6</sub> preparation.

 $UF_5$ . XeF<sub>6</sub> was obtained also when 6.19 m-mole of uranium pentafluoride was allowed to react with 11.91 m-mole of xenon hexafluoride at room temperature. Practically no uranium hexafluoride was formed in this case.

The solid samples rapidly decompose in the air and were therefore handled in a dry box. Xenon was determined both gravimetrically and volumetrically after a weighed part of the sample has been allowed to react with mercury in a closed container at elevated temperature. Another part of the sample was

Anal. Calcd. for UF5. XeF6: U, 41.16; Xe, 22.70; F, 36.14. Found: U, 41.3; Xe, 22.0; F, 35.8.

*I.R. spectra*. Monel 10 cm path length gas absorption cells fitted with silver chloride windows and Zeiss UR-20 spectrometer were used to obtain spectra of gases. The spectra of the solid were obtained by sandwiching thin layers between two silver chloride plates in a dry box and using the same spectrometer. A very strong band was observed at  $667 \text{ cm}^{-1}$ , a weak band at  $616 \text{ cm}^{-1}$ , a band of a medium intensity at  $575 \text{ cm}^{-1}$  and a strong, broad band at  $480 \text{ cm}^{-1}$ . Because the i.r. data on similar materials are rather scarce as yet we could not give the observed bands a reasonable assignment by way of comparison. More work will be needed to elucidate this spectrum.

Magnetic susceptibility measurements. The powdered samples were packed into thin-walled screwcapped KelF containers (4.5 mm o.d., 110 mm height) and measurements were performed using Gouy's method on a Newport Instruments magnetic balance. Diamagnetic corrections were applied using the susceptibilities of uranium hexafluoride[16] and of xenon hexafluoride[17, 18]. Since both susceptibilities are numerically almost equal but opposite in sign, the total diamagnetic correction is negligible. From the slope  $\sigma$  of a plot  $1/\chi_{M^1}$  vs. T, the Weiss constant was calculated since a linear relationship was obtained within the temperature region 90–290°K. The effective magnetic moment,  $\mu_{eff}$ , was then calculated from the expression  $\mu_{eff} = 2.828 \sqrt{\sigma}$ . Its value 1.57 B.M. is close to the spin-only value for one single electron (1.73 B.M.) and much lower than the value calculated under the assumption of the L-S coupling for the  $3/2F_{5/2}$  state (2.54 B.M.). The value of the effective magnetic moment indicates thus that the orbital contribution to the magnetic moment is quenched to a significant extent and that the electronic population of the state is lower than 1. The isolated compound UF<sub>5</sub>. XeF<sub>6</sub> is therefore

Table 1. X-ray powder
diffraction pattern for
$UF_5$ . $XeF_6$

and the second se			
d[Å]	I	d[Å]	i
9.70	s	2.47	w
5.76	w	2.30	w
4.78	m	2.23	w
4.53	vs	2.11	m
4.16	m	2.01	m
4.06	s	1.976	w
3-90	m	1.941	w
3.64	vs	1.883	vw
3.49	m	1.777	vw
3.21	m	1.701	w
3.02	w	1.560	vw
2.93	w	1.510	w
2.82	vw	1.417	vw
2.71	w	1.378	vw
2.57	vw	1.303	w

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a compound of pentavalent uranium. An ionic nature is indicated by the comparison of the measured molar magnetic susceptibility at 200°K ( $1195 \cdot 10^{-6}$  e.m.u.) and that calculated for a mixture of uranium pentafluoride and xenon hexafluoride at the same temperature ( $2200 \cdot 10^{-6}$  e.m.u.). Some other isolated fluorouranates (V) show a very similar magnetic behaviour[19].

X-ray measurements. X-ray diffraction powder patterns were obtained on samples filled in a dry box into thin-walled Kel-F or Pyrex capillaries and using  $CuK_{\alpha}$  radiation with 114.56 mm diameter camera. Line intensities were estimated visually. Due to the difficulties of manipulating the samples, the single-crystal data have not been obtained as yet. In absence of these we did not try to index the powder pattern given in Table 1.

Further work is under way.

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# On the composition of mannitol-borate complex

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**POLYOL-BORATE** complexes form rapidly in aqueous solutions, behave like strong univalent electrolytes, and thus make possible the quantitative determination of  $H_3BO_3$ , for example by addition of mannitol and titration with NaOH-phenolphthalein. In a prevalent concept the principal complex is a borospirane having two polyol molecules per B but a mass of recent evidence indicates that mannitol and borate form only a 1:1 complex[1]. That the complex has a 1:1 composition is reaffirmed by a simple titration experiment described below.

The presence of a 2:1 complex has been inferred mainly from the relationship at equilibrium among  $H^+$ , polyol, and  $H_3BO_3$  concentrations. Indeed, the same pH data for mannitol- $H_3BO_3$  solutions have been interpreted to indicate both a 1:1 complex[1] and a 2:1 complex[2]. Since such divergent conclusions can so readily be reached, the interpretation of data for this equilibrium system is discussed here in some detail. Presented first are two evaluation procedures which yield the correct combining ratio from simultaneous  $H^+$ , polyol (P), and  $H_3BO_3$  (HB) concentrations.

Let the reaction be represented by the equation

$$HB + n P \rightleftharpoons HB \cdot P_n \tag{1}$$

and the corresponding equilibrium constant by

$$\mathbf{K} = \frac{[\mathbf{HB} \cdot \mathbf{P}_n]}{[\mathbf{HB}][\mathbf{P}]^n}.$$
(2)

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