Greenwood & Earnshaw

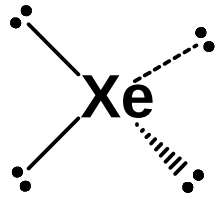
2nd Edition

Chapter 18

The Noble Gases

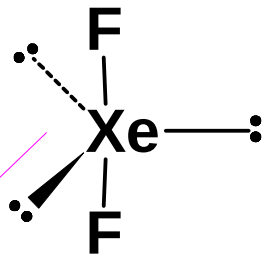
Helium, Neon, Argon, Krypton, Xenon and Radon

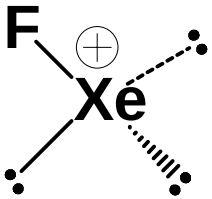
Noble Gas Fluorides



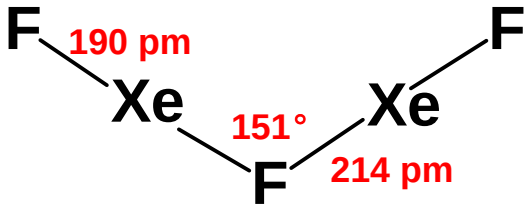
Xe

Δ or $h\nu$ / F_2

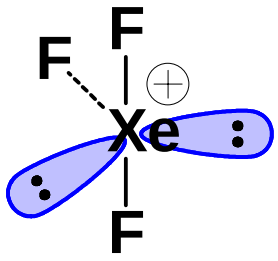




XeF^+ ← $-F^-$ — XeF_2 — XeF^+ → $[Xe_2F_3]^+$

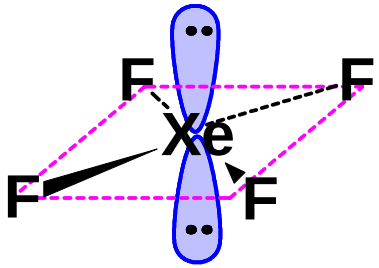


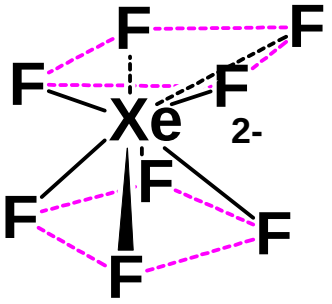
F_2



XeF_3^+ ← $-F^-$ — XeF_4

with difficulty
SbF_5 & BiF_5

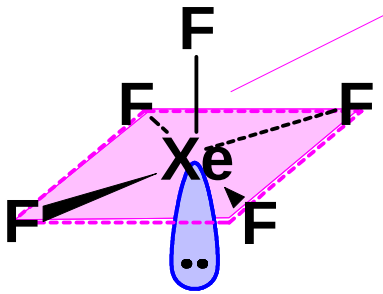




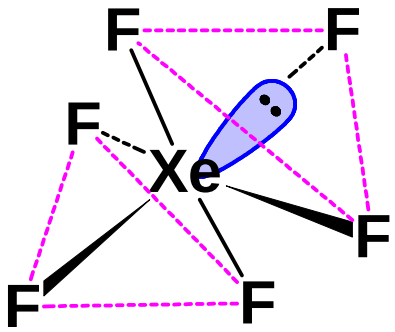
F_2

XeF_5^+ ← $-F^-$ — XeF_6 — $+X^-$ → XeF_7^-

easily loses F^- to weak F^- acceptors



distorted
octahedral



$+X^-$

XeF_8^{-2}

Cs_2IF_8

square antiprismatic,
lone pair not active
stereochemically.

Synthesis of Krypton & Xenon Fluorides

$$Kr + F_2 \xrightarrow[-196\,^\circ C]{\text{X-ray or } \beta} KrF_2$$

Decomposes slowly at 20°C, linear, $d_{Kr\text{-}F}$ 188.9 pm, powerful oxidizing/fluorinating agent.

$$KrF_2 + AgF \longrightarrow AgF_3$$

$$Xe + F_2 \xrightarrow[\text{or } 140\,^\circ C]{h\nu \text{ (sunlight)}} XeF_2$$

Water soluble 25 g/L, stable at 20°C $t^1/_2$ = 7 h, linear, $d_{Xe\text{-}F}$ 200 pm, mp 129°C oxidizing/fluorinating agent.

$$Xe + 5\,F_2 \xrightarrow[\text{Ni vessel}]{\text{6 atm, 140}\,^\circ C} XeF_4$$

$d_{Xe\text{-}F}$ 195.2 pm, mp 117.1°C

$$Xe + 20\,F_2 \xrightarrow[\text{Ni vessel}]{\text{60 atm, 250}\,^\circ C} XeF_6$$

$d_{Xe\text{-}F}$ 184 pm(5), 223 pm(1), mp 49.5°C

Xenon – Oxygen Chemistry

$XeF_2 + HOL \longrightarrow HF + FXeOL \longrightarrow HF + Xe(OL)_2$

L = TeF_5, SeF_5, SO_2F, ClO_3, NO_2, SO_2CF_3 ...

$XeF_4 \xrightarrow[\text{fast}]{H_2O} XeO_3 + Xe + O_2$

explosive

$XeO_{3(aq)}$ is stable, powerful oxidizers
"Xenic Acid"

$XeF_6 \xrightarrow[\text{controlled}]{H_2O} XeOF_4 \longrightarrow XeO_2F_2 \longrightarrow XeO_3$

explosive

O_3, NaOH

$2\ XeF_6 + 16\ OH^- \longrightarrow XeO_6^{-4} + Xe + O_2 + 12\ F^- + 8\ H_2O$

Perxenates are stable, powerful oxidizers

$Ba_2XeO_6 + 2\ H_2SO_4 \longrightarrow XeO_4 + 2\ BaSO_4 + 2\ H_2O$

Very Explosive, mp -35.9°C

Xenon – Nitrogen & – Carbon Compounds

$2\ XeF_2 + 2\ HN(SO_2F)_2 \xrightarrow[0\,°C,\ 4\ days\ -\ 2\ HF]{CCl_2F_2} 2\ FXeN(SO_2F)_2$

$2\ FXeN(SO_2F)_2 \xrightarrow{-10\,°C,\ +2\ AsF_3} \xrightarrow[22\,°C,\ Vacuum\ -\ AsF_5]{} F[XeN(SO_2F)_2]_2^+\ AsF_6^-$

$Xe[N(SO_2F)_2]_2$ is also known.

$XeF^+ + N{\equiv}CR \longrightarrow [FXe{\bullet}N{\equiv}CR]^+\ [AsF_6]^-$

R = H, CH_3, CH_2F, Et, C_2F_5, C_6F_5

$XeF_2 + B(C_6F_5)_3 \xrightarrow[or\ CH_2Cl_2]{CH_3CN} [XeC_6F_5]^+[B(C_6F_5)_3F]^-{\bullet}CH_3CN$

$d_{Xe\text{-}C}$ = 209.2 pm $d_{Xe\text{-}N}$ = 268.1 pm (dative bond)

also known:

$[(CH_3)_3C{-}C{\equiv}C{-}Xe]^+\ BF_4^-$

$[XeF]^+[Sb_2F_{11}]^- \xrightarrow[HF/SbF_5]{Xe} [Xe_2]^+[Sb_4F_{21}]^-$

$d_{Xe\text{-}Xe}$ = 308.7 pm, longest known homonuclear bond.

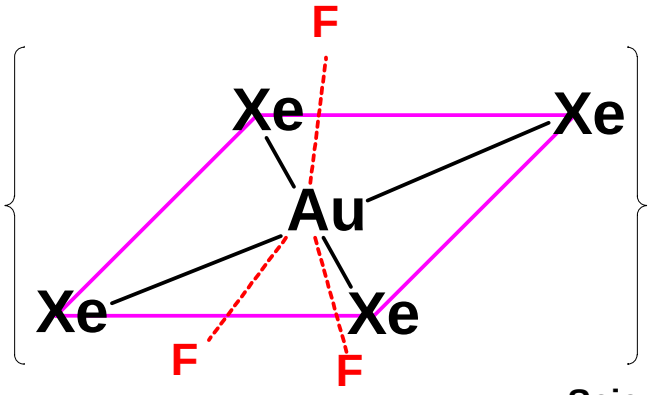
New Chemistry of Xenon

$$XeF^+ Sb_2F_{11}^- + Xe \xrightarrow{HF/SbF_5} Xe_2^+ Sb_4F_{21}^-$$

Dark Green

$d_{Xe\text{-}Xe}$ = 308.7 pm

$$AuF_3 + \underset{\text{excess}}{Xe} \xrightarrow[P_{Xe} = 10\ \text{bar},\ T = 25\,^\circ C]{2:1\ HF/SbF_5}$$



2+

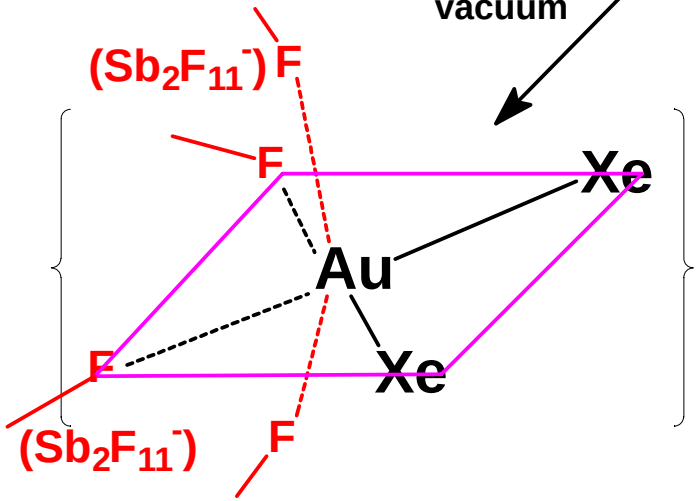
$(Sb_2F_{11}^-)_2$

Science 290, 117 (2000)

$d_{Au\text{-}Xe} \cong 274$ pm

$d_{Au\text{-}F} \cong 267, 295, 315$ pm

$T = -78\,^\circ C$, vacuum

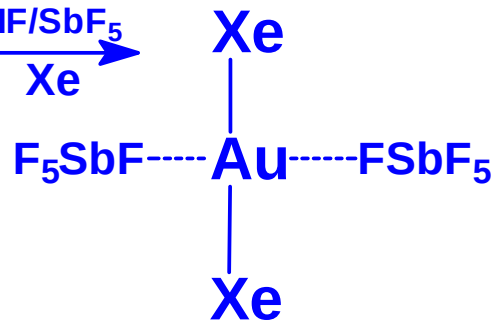


2+

$d_{Au\text{-}Xe} \cong 265, 267$ pm

$d_{Au\text{-}F} \cong 218, 224, 315$ pm

$$Au + XeF_2 \xrightarrow[Xe]{5:1\ HF/SbF_5}$$



$d_{Au\text{-}Xe} \cong 271$ pm

$d_{Au\text{-}F} \cong 216$ pm

Angew. Chem. Int. Ed. 2002, 41, 454.

New Chemistry of the Noble Gases

Irradiation of Molecules in Noble Gas Matrices

Xe:

$$HF \xrightarrow{h\nu} H{-}Xe{-}F$$

$$HCl \xrightarrow{h\nu} H{-}Xe{-}Cl$$

$$H_2O \xrightarrow{h\nu} H{-}Xe{-}OH$$

$$HBr \xrightarrow{h\nu} H{-}Xe{-}Br$$

$$HCN \xrightarrow{h\nu} H{-}Xe{-}CN$$

$$H_2S \xrightarrow{h\nu} H{-}Xe{-}SH$$

Kr:

$$HF \xrightarrow{h\nu} H{-}Kr{-}F$$

$$HCl \xrightarrow{h\nu} H{-}Kr{-}Cl$$

$$HCN \xrightarrow{h\nu} H{-}Kr{-}CN$$

Ar:

$$HF \xrightarrow{h\nu} H{-}Ar{-}F$$

Nature, 406, 874 (2000)