ARSENIC, ANTIMONY AND BISMUTH HALIDES AND OXOHALIDES

References

3+ | "4+" | 5+

As_2O_3 — $AsCl_3$ → **AsOCl**↓

As_2O_3 — HCl (200°) → As_2I_4, cr., dark red, m.p. 136 with dec.; $+ H_2O \longrightarrow As + AsI_3$ (H_2)

	m.p.	b.p.	ΔH	As—Hal (g.)	μ
AsF_3, liq., colrl.	−6	63	−858 [22]	1.71	2.81
$AsCl_3$, liq., colrl.	−16	130	−336	2.16	1.97
$AsBr_3$, cr., colrl.	33	221	−201	2.32	—
AsI_3, cr., red	146	403	−67	2.56	—

MHal →

$M[AsF_4]$, M = K–Cs, $[SCl_3]$, anion: ψ-trig. bipyr., As—F 1.72–1.88
KAs_2F_7 = $K[AsF_4][AsF_3]$, As—F 1.73–1.91 [22]
$[SCl_3]^+[AsF_3Cl]^-$
$KAsCl_4$

SbHal$_5$ →

$[AsF_2]^+[SbF_6]^-$
$[AsCl_2]^+[SbCl_6]^-$

$AsHal_3$ and $SbHal_3$ hyg. substs., sol. in eth., $AsCl_3$ (ε = 13) dissolves S, P; melted $SbHal_3$ readily dissolves $MHal_n$; $AsHal_3 + H_2O \rightleftarrows As(OH)_3 + HHal$ (rate of hydrol. F ≫ Cl > Br > I); $SbHal_3 + H_2O \rightleftarrows Sb(OH)_nHal_{3-n} + HHal \xrightarrow{H_2O} SbOHal$↓; $SbCl_3$ soly. in H_2O ~80%; in struct. and g.: $[:EHal_3]$ mol.: ψ-tetrahedra, ∠HalEHal ≈ 100 (As), ≈ 98 (Sb); EI_3 – layered polymers, isostruct. to $FeCl_3$, As—I 2.55–3.47

As_2O_3 — O_3 (−78°), $As_2O_3 + F_2$ →

AsO_2Cl, cr., colrl., insol. in org. solvs.
$AsOF_3$, g., colrl., m.p. −68, b.p. −26
$(AsOF_3)_n$, powder, wh., hyg.
$AsOCl_3$, cr., colrl., dec. −25 → $(As_2O_3Cl_4)_n$ [32]

M_2AsO_3F; $MAsO_2F_2$
$MAsOF_4$, M = K–Cs, anion $[As_2O_2F_8]$: 2 octahedra with common edge $[O_2]$, As—(F,O) 1.81, As—As 2.66, ∠AsOAs 95 [9]
$M_2[(AsF_5)_2O]$, As—(F,O) 1.72
$M[AsF_5(OH)]$, anion: octahedron, As—(F,O) 1.76

Cl_2 (−105°, UV) →

AsF_5, g., colrl., v. hyg., m.p. −80, b.p. −53, ΔH = −1066, mol.: trig. bipyr. (sp^3d), As—F 1.67 (equ.), 1.71 (ax.); strong F acceptor
$AsCl_2F_3$, m.p. −75
$AsCl_5$, exists in Cl_2 soln. at $t \leqslant -50°$ [15]

$M[AsF_6]$, M = M^I, $[NF_4]$, $[AsCl_4]$, $[SCl_3]$, $[SeCl_3]$, $[TeCl_3]$, $[ClF_4]$, $[ClO_2]$, $[IO_2]$, $[IF_6]$, [XeF], $[Xe_2F_3]$, $[Xe_2F_{11}]$, $[XeF_5]$, anion: octahedron, As—F 1.63–1.70, stab. to the act. of H_2O
M_2AsF_7
$M[AsCl_6]$, M = $[PCl_4]$, $[Et_4N]$, cr., orange

$ECl_n + Cl_2$ →

$AsF_3(NO_3)_2$

$[AsF_4]^+[PtF_6]^-$
$[AsCl_4]^+X^-$, X = PCl_6, $AlCl_4$, $AuCl_4$, AsF_6, SbF_6, v. hyg.
$[AsBr_4]^+X^-$
$[AsI_4]^+X^-$, unstab. [42]

E — Hal_2

$Sb_3O_2F_5$; SbOF; Sb_3O_4F; SbOCl↓; $Sb_4O_5Cl_2$↓; $Sb_8O_{11}Hal_2$, $Sb_4O_5Br_2$↓; Hal = Cl–I; Sb_3O_4I; Sb_5O_7I
Struct.: ψ-tetrahedra, trig. bipyr. and Hal^-, Sb—O 1.9–2.5 [25]
SbEHal, E = S–Te, Hal = Cl–I, semiconductors

	m.p.	b.p.	ΔH	Sb–Hal (g.)
SbF_3, cr.,colrl.	292	319, subl.	−916	1.88
$SbCl_3$, cr., colrl.	73	233	−382	2.33
$SbBr_3$, cr., colrl.	97	289	−260	2.49
SbI_3, cr., red, non-hyg.	171	401	−100	2.72

$SbHal_3$ (Hal = F–Br) isostruct. to YF_3, SbI_3 isostruct. to PI_3, Sb—Hal 1.92 (F), 2.34 (Cl), 2.49 (Br), 2.72 (I), ∠HalSbHal 87 (F), 99 (I). $SbHal_3$ sol. in ROH, bz., Diox;
· ***n*** **L**, L = Dipy, C_6H_6, $C_{10}H_8$ – π-complexes.

MHal →

$M[SbF_4]$; Na_2SbF_5; KSb_2F_7; $Li_3Sb_2F_9$
$NaSb_3F_{10}$; $K[F(:SbF_3)_4]$; $K_3Sb_4F_{15}$
$Na_3Sb_5F_{18}$; anion: ψ-trig. bipyr. (disphenoid) or octahedra, Sb—F 1.96–2.06
$M_4Sb_4F_{16}$, anion: $[:SbF_3F_{2/2}]$ ring
$M[SbCl_4]$; $M_2[SbCl_5]$; $M_3[SbCl_6]$; Cs_4SbCl_7
Cs_5SbCl_8; $M_3Sb_2Cl_9$; $Cs_8Sb_2Cl_{11}$; $M_7Sb_3Cl_{16}$
$Tl_2Sb_3Cl_{11}$, anion: octahedra, ψ-octahedra, Sb—Cl 2.4–3.2
$RbSbBr_4$; $K_2Sb_2Br_9$; M_3SbBr_6, anion: octahedra (!), Sb—Br 2.79
K_2SbI_5; $Cs_3Sb_2I_9$, anion: octahedra, Sb—I 2.86–3.20
$MSbI_4$, in anion: octahedra [3]

$SbCl_n$, $n \leqslant 3$, exp. Sb, graphite-like mass, exp. at friction, d = 5.8, struct. – at. Sb, $[SbCl]^{2+}$, $[SbCl_2]^+$, Cl^-

cat. Red (≪ 0°) →

HCl (conc.) — Sb_2S_3

SbF_4 = $[Sb_2^{III}F_4]^{2+}[Sb^VF_6]_2^-$

$Sb_{11}F_{43}$ = $[Sb_6^{III}F_{13}]^{5+}[Sb^VF_6]_5^-$, cation: chain of 2 completed and 3 $[:SbF_3]$ ψ-tetrahedra, Sb—F 1.7–1.9 (termnl.), 2.06–2.2 (br.)

$M_2[Sb^VF_6][(Sb^{III}F_2)(Sb^VF_6)_2]$
$Sb_2F_4Cl_5$ [8]
$[SbCl_4]$, brn. soln.

M_2SbCl_6, M = Rb, Cs, cr., blk., diamagn.; $+ H_2O \longrightarrow M_3[SbCl_6] + M[SbCl_6]$
M_2SbBr_6, cr., blk., diamagn., isostruct. to K_2PtCl_6, anions: $[Sb^{III}Hal_6]$ and $[Sb^VHal_6]$

$(SbOF_3)_n$; SbO_2F
SbO_2Cl
$SbOCl_3$↓,
yel. subst., hyg., insol. in org. solvs.;
$+ H_2O \longrightarrow Sb_2O_5 \cdot nH_2O$↓

↑ **H_2O**

Hal_2; BrF_5 — E

MSbOF$_4$
$M_2Sb_2OF_{10}$
$M[SbF_5(OH)]$, Sb—F 1.83–1.92 [16]
$Na[SbF_4(OH)_2]$
$H[SbF_{6-n}(SO_3F)_n]$, n = 0–3

	m.p.	b.p.	Sb—Hal	
$(SbF_5)_n$, oil, colrl., viscous, weakly hyg.	8.3	149	1.82 termnl.	2.02 br.
SbF_3Cl_2	—	—	—	—
SbF_2Cl_3	—	—	—	—
$SbFCl_4$	—	—	equ.	ax.
$SbCl_5$, liq., colrl.	3	102/vac.	2.29	2.34
$SbBr_5$ (?)	—	—	2.31	2.43

ΔH SbF_5 = −439, solv. for S, Se, Te; v. strong F^-acceptor; $SbCl_5$ – strong chlorinating agent. In liq. $(SbF_5)_n$ (n = 5–10): chains of $[SbF_4F_{2/2}]$ octahedra, in struct.: tetramers of *cis*-$[SbF_4F_{2/2}]$ octahedra[11], in g.: $[SbF_3F_{2/2}]_3$ rings.
$SbHal_5 \xrightarrow{t} :SbHal_3$ (equ.) $+ Hal_2$ (ax.); $+ H_2O \longrightarrow SbOHal_3$ (equ.) $+ 2\,HHal$ (ax.)
$SbCl_5 \cdot L$, L = NOCl, $POCl_3$, SO_2, mol.: octahedra

$[SbF_4]^+[SO_3F]^-$
$[SbCl_4]^+X^-$,
X = SbF_6, $SO_4/2$, Hal
$[SbBr_4]^+X^-$,
X = $Sb(OTeF_5)_6$ [44]

$SbF(NO_3)_4$
$SbF_3(NO_3)_2$

$M[SbF_6]$; $M[Sb_2F_{11}]$, M = M^I, $[NF_4]$, $[AsCl_4]$, $[SbCl_4]$, $[O_2]$, $[S_8]/2$, $[S_{16}]/2$, $[SF_3]$, $[H_2F]$, $[Cl_3]$, $[HalF_2]$, $[HalF_4]$, [KrF], Xe/n, [XeF], $[XeF_3]$, $[XeF_5]$, $[XeOF_3]$, $[Xe_2F_{11}]$, anions: octahedron or 2 octahedra with common vertex, Sb—F 1.8–1.9 (termnl.), 2.0–2.1 (br.), ∠SbFSb 150
$M[Sb_3F_{16}]$, M = $[PF_4]$, $[Br_2]$, anion: chain of 3 octahedra, $[SbF_4F_{2/2}]$-*trans* [16] in the centre
$M_2[SbF_7]$; $H_3[SbF_8]$, Sb CN 7 and 8; **$[BrF_4]^+[Sb_7F_{36}]^-$**
$HSbCl_6 \cdot 3H_2O$, cr., grn., hyg.; **$[H_{14}O_6][SbCl_6]_2 \cdot nH_2O$**
$M[SbCl_6]$, M = M^I, $[SCl_3]$, [NO], $[ICl_2]$, [PyH], Sb—Cl ≈ 2.32
$M[(SbCl_5)_2X]$, X = F, CN, N_3
$H[SbBr_6] \cdot 3H_2O$; $M[SbBr_6]$, in octahedron Sb—Br 2.56
$Cs[SbI_6]$ [14]

MF + BrF_3 →

E_2O_3 — BrF_3 → **BiF_5**, needles, colrl., m.p. 151, b.p. 230, v. strong fluorinating agent, in α-UF_5 struct.: chains of *trans*-$[BiF_4F_{2/2}]$ octahedra, Bi—F 1.90 [17]

Bi — F_2 (500°); ClF_3 (350°) →

MF + F_2 (p); $[NH_4]BF_4$ →

K[BiOF$_4$]
$M[BiF_6]$, M = Li–Cs, Mg–Ba/2, $[BrF_2]$, $[O_2]$, $[H_3O]$, $[XeF_3]$, NF_4 [17], $+ H_2O \longrightarrow O_2 + H_2O_2 + \ldots$

Bi — $BiHal_3$; Hg_2Cl_2 — aq. reg. →

$Bi_{24}Cl_{28}$ (≈ "BiCl") = **$[Bi_9]_2^{5+}[Bi^{III}Cl_5]_4^{2-}[Bi_2^{III}Cl_8]^{2-}$**, cr., brn., hyg.,
m.p. 163; $\xrightarrow{300°}$ Bi + $BiCl_3$;
Bi_6Cl_7
$Bi_{24}Br_{28}$, semiconductor
BiI, m.p. 318 with dec.
Bi_7I_2; Bi_9I_2
$Bi_{10}I_3$, m.p. 295 [1]

BiOF; $Bi_7O_9F_3$; Bi_3O_4F; $Bi_{13}O_{19}F$
BiOCl; $Bi_4O_5Cl_2$; Bi_3O_4Cl; $Bi_{12}O_{17}Cl_2$; $Bi_{24}O_{31}Cl_{10}$
BiOBr; $Bi_{12}O_{15}Br_6$; Bi_3O_4Br; $Bi_{12}O_{17}Br_2$; $Bi_{24}O_{31}Br_{10}$
BiOI; Bi_5O_7I, struct.: $[Bi_{10}O_{14}]_n^{2n+}$ columns, Bi CN 7, 8 and 9, Bi—O 2.09–2.86.
Struct. of other oxohalides: HalBiOBiHal... layers (in BiOHal) or $[Bi_{12}O_{15}]^{6+}$ of ψ-octahedra, Bi—O 2.0–2.7, Bi—Hal 3.05–3.20 (Cl), 3.19 (Br), 3.37 (I), Bi—Bi 3.73 [29]
BiSHal, BiSeHal, Hal = Cl–I, Bi CN 8, Bi—S 2.8–3.3, Bi—Cl 2.7–3.5

$MBi_3O_4Cl_2$
$LiBi_2O_3Cl$
$BaBiO_2Cl$

H^+ | H_2O

[31]	m.p.	b.p.	ΔH	Bi—Hal (g.)
BiF_3↓, cr., grey	727	900	−899	—
$BiCl_3$, cr., wh., darkening in light	234	447	−379	2.48
$BiBr_3$, cr., yel.	219	461	−260	2.63
BiI_3↓, cr., brn., sol. in I^-, $S_2O_3^{2-}$, AsO_3^{3-} presence.	408	439 (subl.)	−109	—

In g.: $[:BiHal_3]$ mol.: ψ-tetrahedra, ∠HalBiHal ≈ 100, in ion struct.: BiF_3 and $BiCl_3$ (YF_3 type), Bi CN 8+1, in $BiBr_3$ struct. (α- and β-): distort. octahedra; BiI_3 isostruct. to $FeCl_3$, Bi—Hal 2.23–2.50 (F), 2.50–2.34 (Cl), 2.66–3.32 (Br), 3.07 (I)
$BiCl_3 \cdot nL$, L = NO, NO_2, NOCl

$MBiF_4$, struct.: $[BiF_9]$ grs., Bi—F 2.19–2.86
K_2BiF_5; K_3BiF_6; KBi_2F_7; KBi_3F_{10}
$MBiCl_4$; $M_2[BiCl_5]$; M_3BiCl_6; Cs_4BiCl_7
$Rb_3Bi_2Cl_9$; $Rb_7Bi_3Cl_{16}$; $M_2Bi_2Cl_8$, anion: 2 ψ-octahedra with common edge
M_2BiBr_5; M_3BiBr_6; $Cs_3Bi_2Br_9$
$M_4[Bi_2Br_{10}] \cdot 4H_2O$; $M_7[BiBr_6][Bi_2Br_{10}]$, anions: octahedra or ψ-octahedra, Bi—Hal 2.6–2.9 (Cl), 2.7–3.0 (Br)
$KBiI_4$; $HBiI_4 \cdot 4H_2O$; $M_3[Bi_2I_9]$
$Rb_5I(I_3)[BiI_6]$, in anions: octahedra, Bi—I 2.9–3.2 [7]