References

Bi_2O_3, cr., yel., $\overset{t}{\rightleftarrows}$ brn., bismite, d = 8.2–8.9, m.p. 824 (rhomb.), 860 (tetrag.), b.p. 1890, $\Delta H = -577$, sol. in ac.;
Bi_2O_3 melt dissolves Pt; α-, monocl. $\xrightarrow{729°}$ δ-, cub. $\xrightarrow{824°}$ liq.
β-, tetrag. (20–639°) + γ-, cub. (300–650°) $\xrightarrow{\text{cool}}$ (metastab. phases)
Structures for all forms: framework of octahedra [43]

↑ 150°

BiO(OH)
↑ 100°
$Bi(OH)_3$↓, wh., sol. in ac. and conc. alk.
$[Bi_2O(OH)_2](OH)_2$, struct. analogue of sulfate

BiO(ClO_4), sol. in H_2O [23, 28]
$[Bi_6O_4(OH)_4](ClO_4)_6 \cdot 7H_2O$
$[Bi_2O(OH)_2]SO_4$, cation: chain of octahedra and pentagons, Bi—O 2.16–2.74
$Bi_2O(SO_4)_2$, Bi CN 7 and 8, Bi—O 2.2–3.0
$[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4H_2O$
↓ H_2O 50°
$[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$
$[Bi_6O_4(OH)_4(NO_3)(H_2O)](NO_3)_5$, cation: [$Bi_6$] octahedron, μ_3-O and μ_3-OH – over centres of faces, Bi—Bi ~3.6, [:BiO_4] – disphenoid
$Bi_2O_2CO_3$, 400° ⟶ Bi_2O_3, Bi—O 2.3

↓↑ H_2O

$Bi(ClO_4)_3$, $\cdot 5H_2O$
$Bi(IO_3)_3$↓
$Bi_2(SO_4)_3$, needles, hyg., m.p. 710 (p)
$Bi(NO_3)_3$,
$\cdot 5H_2O$, dec. 80, sol. in eth., ac., Bi CN 10, Bi—O 2.32–2.99
$BiPO_4$↓, sol. in HCl
Bi[VO_4], pucherite
Bi[AsO_4], rooseveltite, isostruct. to monazite
$Bi_2(C_2O_4)_3$↓; **$Bi(HCOO)_3$**
$Bi(OCOCH_3)_3$, Bi CN 9
$Bi_4(SiO_4)_3$, eulytine [33]

Bi_2O_2S, blk., struct.: framework of antiprisms [$Bi_4O_4S_4$], Bi—O 2.31, B—S 3.2, Bi—Bi 3.47 [33]
Bi_2O_2Se

Bi_2S_3↓, dark-brn., SP = 10^{-72}, bismuthinite (bismuth glance), cr., blk., m.p. 685 with dec., $\Delta H = -156$, sol. only in conc. HNO_3, isostruct. to Sb_2S_3, Bi CN 7
Bi_2Se_3, cr., blk., m.p. 710, b.p. 1007
Bi_2Te_3, m.p. 580, b.p. 1172, $\Delta H = -79$
$PbBi_2S_4$, galenobismutite } double sulfides
$CuBiS_2$, emplectite } (not sulfosalts)

Bismuthates (III)
$M_3[BiO_3]$, light-yel., **$CsBiO_2$**, in struct.: ψ-tetrahedra or chains of [$BiO_{4/2}]_\infty$ tetrahedra Bi—O ~2.05–2.34
$Ba_2Bi_2O_5$ [21]

$M_2[Bi(ClO_4)_5]$; $MBi(ClO_4)_4$
$K[Bi(SO_4)_2]$
$K_3[Bi(SO_4)_3]$
$M_3[Bi(S_2O_3)_3]$, M = Na, K↓, NH_4↓, Sr/2↓, Ba/2↓, cr., yel.
$M_3^{II}[Bi(NO_3)_6]_2 \cdot 24H_2O$
$K_2[Bi(HCOO)_5]$, Bi CN 10, Bi—O 2.47–2.73 [5]

H_2SO_4 (conc.), N_2O_4, HNO_3 (conc.) — Bi

Rb[Bi(SCN)$_4$]

$M_2S_n + S$ (t)

MBiS$_2$, struct. NaCl type with statistical distribution of M
$K_8Bi_2S_7$
KBi_3S_5, semiconductor; struct.: units of octahedra with common edges
$K_2Bi_4S_7$ [34]

As_2O_3 — O_2 (t, p); Sb_2O_3 — air (400°), 1000°; 940° Sb_2O_5

$E_2O_4 = E^{III}E^{V}O_4$, E = As, Sb, Bi

AsO_2
$SbAsO_4$

SbO_2↓, cr.
colrl., $\xrightarrow{t}$ yel., dec. 1060, $\Delta H = -908$
Sb_6O_{13} [27]

BiO_2,
powder, brn., m.p. 305 with dec.

$BiSbO_4$ **Bi_4O_7** [27]

Struct.: layers of [:$E^{III}O_3$] and [$As^{V}O_4$] tetrahedra or [$Sb^{V}O_6$] octahedra

MOH (t)

$M_2Sb_2O_5$ =
= $M_2[Sb^{III}O][Sb^{V}O_4]$
Ca_3SbO_5, dec. 1100 [24]

$BaBi^{III}Bi^{V}O_5$, perovskite type struct. [24]

t ($-O_2$)

As_2O_5, glass, colrl., hyg., dec. 400, $\Delta H = -928$; rhomb. $\overset{225°}{\rightleftarrows}$ tetrag., struct.: framework of tetrahedra and octahedra, As—O 1.68 and 1.82 [35]

H_2O ↕ 120° ($-H_2O$)

$H_3AsO_4 \cdot 0.5H_2O$, cr., hyg., colrl., m.p. 35, dec. 160, readily sol. in H_2O, $K_1 = 10^{-2}$, $K_2 = 10^{-7}$, $K_3 = 10^{-12}$
$H_5As_3O_{10}$, struct.: chains of octahedra and tetrahedra with common vertices
$H_3AsO_4 \cdot 2H_2O$

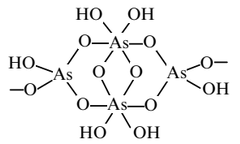
E — HNO$_3$ (conc.); MClO$_3$; MNO$_3$ (t); aq.reg.

Arsenates (V), cr., colrl. [39]

ortho-	di (pyro-)	tri-	meta-
$Na_2[AsO_3(OH)] \cdot 12H_2O$			
$NaH_2AsO_4 \cdot nH_2O$ n = 1, 4 $\xrightarrow[(-H_2O)]{90°}$	**$Na_2H_2As_2O_7$** **$Ba(H_3As_2O_7)_2$** $\xrightarrow[(-H_2O)]{135°}$	**$Na_3H_2As_3O_{10}$** **$K_5As_3O_{10}$** $\xrightarrow[(-H_2O)]{230°}$	**$NaAsO_3$** m.p. 615

KH_2AsO_4, m.p. 288
$M_2HAsO_4 \cdot nH_2O$, M = Na (n = 7, 12), K (n = 1)
$M_2^{II}AsO_4(OH)$, M = Cu (olivinite), Zn (adamite)
$CaHAsO_4$, $\cdot 2H_2O$, pharmacolite; **M_3AsO_4**, M = Li, Na ($\cdot 12H_2O$), K, NH_4 ($\cdot 3H_2O$), Ba/2↓, Pb/2↓
$M_3^{II}[AsO_4]_2 \cdot 8H_2O$, M = Zn (koettigite), Co (erythrite, annabergite)
$Ca_2Mg(AsO_4)_2 \cdot 2H_2O$, belovite
Ag_3AsO_4↓, brn., SP = 10^{-20}
NH_4MgAsO_4↓ $\xrightarrow{t}$ **$Mg_2As_2O_7$**

$Ba(AsO_3)_2$↓, struct.: chains or rings of tetrahedra, As—O 1.62–1.81 (struct. analogues of phosphate)
$M^{II}(AsO_3)_2$, M^{II} = Ca, Cd, Pb, Co, struct.: framework of [AsO_6] octahedra
$Na_3H_5As_4O_{14}$, struct.: framework [AsO_6] octahedra, and [AsO_4] tetrahedra, As—O 1.77–1.88 and 1.64–1.73



$[H_6As_4O_{14}]^{2-}$

$BaH_6As_4O_{14}$

H_2S (H^+)

As_2S_3 — S_n^{2-}, S + OH⁻

As_2S_5↓, yel., $\xrightarrow{500°}$ As_3S_3 + S, $\Delta H = -146$, in g. – As_4S_{10} mol., struct. analogues of P_4O_{10}

OH^-, CO_3^{2-} / S^{2-} / H^+

$M_3[AsO_3S]$ [10]
$M_3[AsOS_3]$; $Na_3[AsO_2S_2] \cdot 11H_2O$
M_3AsS_4, M = Na ($\cdot 8H_2O$), K, NH_4, Cu/2 (luzonite), cr., colrl., anion: tetrahedron, As—S 2.14–2.23, As—O 1.67

Sb_2O_5↓, cr., yel., struct.: framework of octahedra with common edges and vertices, $\xrightarrow{600°}$ Sb_6O_{13} $\xrightarrow{940°}$ SbO_2, $\Delta H = -1008$, sol. in alk., conc. HCl, M_2CO_3, M_2S [35, 36]

Sb_2O_3 — O_2 (700°, p)

420°

H[Sb(OH)$_6$] $\underset{H_2O}{\rightleftarrows}$ **$Sb_2O_5 \cdot nH_2O$**↓
in soln. n = 3.9 – 0.45 (< 290°) [36]

MOH

Antimonates (V) [13]
M[Sb(OH)$_6$], M = Li, Rb, Cs, Na↓, K↓, NH_4↓, Ag↓, [$Mg(H_2O)_6$]/2↓, NaCl type struct., anion: octahedron, Sb—O 1.97
$M_2Sb_2O_5(OH)_2 \cdot nH_2O$, M = Na ($n$ = 1)↓, K (n = 4)
$MSbO_3$↓; **$K_2Sb_4O_{11}$; MSb_5O_{13}**
$K_3Sb_5O_{14}$; $M_4[Sb_8O_{12}(OH)_{20}]$ [38]
$M^{II}Sb_2O_6$↓;
$M_2^{II}Sb_2O_7$↓; **$M_7^{II}Sb_2O_{12}$**
$M^{III}SbO_4$↓, **M_5SbO_5,**
anions: condensed octahedra, Sb—O 1.8–2.1 [38]
$K_{11}[SbNb_{12}O_{38}] \cdot 14H_2O$

$Bi_2O_n \cdot xH_2O$↓, n = 4–5, coloured from yel. to blk., easily evolves O_2
$Bi_2O_{4.7} \cdot 3H_2O$ [37]

Bi_2O_3 — KClO$_3$; MOH ⇅ HNO$_3$

Bismuthates (V) [38]
$NaBiO_3$↓, cr., yel.
$KBiO_3$, red-viol.
$Ba(BiO_3)_2 \cdot 4H_2O$, orange
$AgBiO_3$↓, blk.
M_3BiO_4; Li_5BiO_5, anion: octahedron, Bi—O 2.07
Li_7BiO_6, ionic conductor, struct.: [BiO_6] octahedra

Bi_2O_3 — $M_2O_2 + O_2$(t)

$SbO(NO_3)_3$, cr., yel.
$SbO(PO_4)$, struct.: framework of [SbO_6] octahedra and [PO_4] tetrahedra, Sb—O 1.90–1.99;
$\xrightarrow{945°}$ $SbPO_4$ [41]

550°

$HSb(PO_4)_2 \cdot 4H_2O$ [41]
M[$Sb(PO_4)_2$],
M = Li–Cs

$M_2[AsO_3(OOH)]$
$M_2[As_2O_4(O_2)F_2]$ [45]

H_2S (H^+, $-Sb_2S_3$↓ $-S$↓)

Sb_2S_5 (?)↓, orange, cr., dec. 170 [12]

S^{2-} ⇄ H^+

$M_3[SbS_4]$, M = Na ($\cdot 9H_2O$, Schlippe's salt), K ($\cdot 4.5H_2O$), cr. yel., anion: tetrahedron, Sb—S 2.38