**4 + ($d^1$)** **5 + ($d^0$)**

(3.5 – 3.75) +
**$V_nO_{2n-1}$**
**$V_3O_5$**, struct. analogue of $Ti_3O_5$ [42]

$K_2O(-O_2)$

**$VO_2$**, cr., hyg., m.p. 1545, b.p. ~ 2700, $\Delta H = -720$, sol. in ac. and alk., struct.: distort. rutile type, paramorontrosite; · **2/3 $H_2O$**, doloresite [34]

$(COOH)_2$; $V_2O_3$(t); $H_2$; $NH_3$

**$VO(OH)_2$**↓, yel., sol. in ac. and alk., duttonite [12]

445° ($N_2$) — $NH_4VO_3$

750°

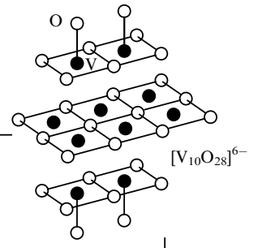
4.33 +
**$V_6O_{13}$**, cr., blue-blk., dec. 650, in struct. octahedra, V — O 1.6 – 2.3 [34]
**$V_4O_9$; $V_3O_7$** = $V^{IV}[V_2^VO_7]$

4.66 + 4.8 +
**$V_3O_7 \cdot H_2O$; $V_2O_{4.8} \cdot nH_2O$**, $n = 0.5$, 3.5, blk., corvusite [30]

$O_2$ (t, $-VO_2$) — V

**$V_2O_5$**, cr., orange, m.p. 680, dec. 700, $\Delta H = -1573$, sol. in $H_2O \approx 0.04\%$, sol. in ac. and alk., volatile with $H_2O$ vapour (⇆ $H_4V_2O_7$ g.), $V_2O_5$(liq.) ⇆ $VO_2^+ + VO_3^-$ (conductor), struct.: double chains of [$VO_5$] tetrag. pyramids, V = O 1.58, V – O 1.78 – 2.0 (4 bonds); · **$nH_2O$**, $n = 1$ ("$HVO_3$", navajoite), 2 ("$H_4V_2O_7$"), 3 ("$H_3VO_4$") – fibrous cr. [28]

$NH_4VO_3$ (t, $-NH_3$, $-H_2O$)




$MVO_3 + V_2O_4$; M

**$M_xV_2O_5$**, M = Li – Cs, $NH_4$, Cu, Ag, $0 < x < 1$, bronzes, in struct.: at. of V(IV) and V(V), CN 5 (tetrag. pyramid), V — O 1.53 – 1.98 [18]; **$M_5[V_{15}O_{36}]$, $M_8[V_{19}O_{41}(OH)_9]$**, anions: clusters, sphere and ellipse, V(V) – V(IV) ~ 2.94

MOH
$H^+$

HX (conc.)
MOH

$M_2O_2 + MOH$(t) — V

**Vanadates (V)** [24]
**$M_6V_{10}O_{28} \cdot nH_2O$**, M = Na ($n = 18$), Ca/2 (17, pascoite), Ba/2 ($n = 19$) cr., orange anion of 10 distort. octahedra [$VO_6$] with common edges, V — O 1.68, 1.80, 1.90, V — V 3.04 – 3.32
**$K_3V_5O_{14}$; $[R_4N]_3HV_4O_{12}$; $K_5V_3O_{10}$; $MV_3O_8$**
**$M_4V_2O_7$**, M = Na ( · $H_2O$), K ( · 2 $H_2O$), Ag↓
**$MVO_3$**, M = Na, K (m.p. 520), Cs, $NH_4$ (dec.30), Ag↓, Ba/2 ( · $H_2O$), struct.: condenced tetrahedra, trig. bipyrs., tetrag. pyrs. or octahedra, V — O 1.62 – 1.97
**$M_3[VO_4]_n$**, M = Na (m.p. 866), K ( · 2 $H_2O$), Ag↓, Sr, Ba, Al ( · 3 $H_2O$, steigerite), Sc, Ln, Bi, Fe(III) (fervanite), Cu(II) ( · 3 $H_2O$, volborthite); struct.: isolated tetrahedra, V — O 1.75 [isostruct. to $M_3(PO_4)_n$]
**$Pb_5[VO_4]_3Cl$**, vanadinite, yel.-red, isostruct. to apatites
**$K(UO_2)[VO_4] \cdot 1.5H_2O$**, carnotite
**$M_n[VW_{12}O_{40}]$; $K_4[V_2W_8O_{31}]$; $Mn[PV_xW_{12-x}O_{40}]$; $M_7[PV_{12}O_{36}]$; $M_6[H_3PV_{14}O_{42}]$, $(NH_4)_5H_3Mn_3V_{12}O_{40} \cdot 15H_2O$** [29]

3.5 +
**$V_2O_2(OH)_3$**, haeggite

**Vanadates (IV)** (vanadites), [44] cr., yel. or brn.
**$Na(VO)_2(OH)_5$; $K_2V_3O_7 \cdot 2.66H_2O$**
**$M_4^IVO_4$** (ortho-)
**$M_3^{II}VO_5$; $M_2^{II}VO_4$; $M_2^IVO_3$** (meta-)
**$M_2^IV_2O_5$**, (pyro-), from melts.
**$M_2V_4O_9 \cdot 7H_2O$** (tetra-, hypovanadates), cr., formed from solns.
**$CaV_4O_9 \cdot 5H_2O$**, simplotite
**$H_8[Mo_3V_3O_{19}]$; $M_3[Mo_2V_4O_{19}H_7]$**, blue

$MN_3(-N_2)$

**Vanadyl (IV) salts, O = $VX_2$** [31]
**$VO(ClO_4)_2 \cdot 5H_2O$**
**$VOSO_4$**↓, cr., grn., · **$nH_2O$**, $n = 1 - 3$, 5 (= $[VO(H_2O)_5]SO_4(H_2O)$), 6 blue, readily sol. in $H_2O$, alc.; · **0.5 $H_2SO_4$**; · **$nM_2SO_4$**, $n$ = 1, 2, cr., bl.
**$VOSeO_3$**, light-grn.
**$(VO)_3(PO_4)_2 \cdot 9H_2O$**
**$VO(HPO_4) \cdot nH_2O$**
**$VO(H_2PO_4)_2$**, blue
**$(VO)_2P_2O_7$** [46]
**$VO(C_2O_4) \cdot nH_2O$**, $n$ = 2, 4
**$VO(RCOO)_2$** [39]
In salt struct.: octahedral [$VOX_5$] ion, V = O 1.58 – 1.67, V — O 2.0 – 2.2

MOH ⇄ HX

$[VO_2]^+X$, X = $NO_3$, $ClO_4$, Cl, cr., red, strong Ox agent, exists at pH < 1 **$[VO_2(RCOO)]_4$** [19]

V — $N_2O_4(-NO)$

**$V_2O_3(SO_4)_2 \cdot 2H_2O$**, in struct. [$VO_6$] octahedra and [$SO_4$] tetrahedra, V — O 1.56 (termnl.), 1.78 (br.) [47]

$O_3$; $ClO_3$

**$Ba[VO(PO_4)]_2 \cdot 4H_2O$** [48]
**$K_2[VO(P_2O_7)]$**, anion: tetrag. pyramid
**$Sr[VO(AsO_4)]_2$**, struct.: chains of octahedra, V = O 1.63, V — O ~2.0; [48]
**$Na_{14}[V_{18}O_{42}(CO_3)] \cdot 28H_2O$**
**$(NH_4)_2[VO(C_2O_4)_2] \cdot 2H_2O$**, cr., blue

$C_2O_4^{2-}$ ($-CO_2$)

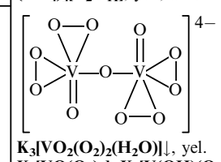
**$M[VO_2(SO_4)]$** [21]
**$M_3[VO_2(C_2O_4)_2]$**-*cis*, octahedron, V = O 1.63 and 1.64, V — O 2.00 (*cis*- to O) and 2.23 (*trans*-)
**$M_3[VO_2F_4]$**, struct.: linear gr. [O = V = O]
**$M_2[VO_2F_3]$, $Cs_3[(VO_2)_2F_5]$**
**$M[VO_2Cl_2]$**, M = K – Cs, V = O 1.56 and 1.60, V — Cl 2.23 [22]

**$(NH_4)_4[V_2O_3(SO_4)_4]$** [22]
**$K[VO(SO_4)_2]$**, in [$VO_6$] octahedron V = O 1.52 (termnl.), 1.82 (br.) [47]

$[O{=}V(O)_2]^+$
**$[VO_3]^+X^-$**, peroxovanadyl(V) salts, cr., red-brn.

$H^+$

**$M[VO_2(O_2)] \cdot 0.5H_2O$**
**$M_2[V_2O_2(O_2)_4(H_2O)]$**
**$(NH_4)_4[V_2O_{11}]$**, yel., anion:




**$K_3[VO_2(O_2)_2(H_2O)]$**↓, yel.
**$K_3[VO(O_2)_3]$; $K_2[V(OH)(O_2)_3]$**
**$M_3[V(O_2)_4] \cdot nH_2O$**↓, M = K (blue-viol.), $NH_4$ (colrl.)
**$M_n[VO_m(O_2)_pL_{7-m-2p}]$**, M = K, $NH_4$; L = $NH_3$, Dipy, $C_2O_4$, F, $CO_3$, anion: pentag. pyramid, V at. shifted to O at. over equ. plane, V = $O_{ax.}$ 1.61, V — OO 1.9, O — O 1.43 – 1.50 [27]

$H_2O_2$
($H^+$)
(OH⁻)
+L

**$VOF_2$**, cr., yel.
**$VOCl_2$** cr., grn., subl., dec. 300; · **2.5 $H_2O$**
**$VOBr_2$**, cr., yel., dec. 180
**$VOI_2 \cdot 2.5H_2O$**, cr., brn.
$VOHal_2$, hyg., readily sol. in $H_2O$, alc.
**$VO(NH_2)_2$**, blk., $\xrightarrow{t}$ VO(NH) $\xrightarrow{t}$ $(VO)_3N_2$ ⟶ VON
**$VO(OR)_2$**, brn. powders [13]

**$M_3[VOF_5]$; $Cs_3[V_2O_2F_7]$; $Cs[VOF_3] \cdot 1/2H_2O$**
**$M_2[VOF_4]$; $K_2[VOF_4(H_2O)]$**, bl.
**$M_2[VOCl_4]$; $Cs_3[VOCl_5]$**, anion: chains of octahedra, V — O 1.9 – 2.3, V = O 1.58 – 1.68, V — F 1.88 – 2.19
**$K_3[VO(CN)_5]$**, anion: octahedron, V = O 1.64, V — C 2.31 (ax.), 2.14 (equ.) [15]
**$M_2[VO(NCS)_4]$**

$V_2O_5$ — $ClO_3$
$V_2O_3$ — $Hal_2$

| **$VOX_3$**, yel. hyg. subst | m.p. | b.p. | $\Delta H$ |
|---|---|---|---|
| **$VO(ClO_4)_3$**, liq. | 22 | 33.5 | — |
| **$VO(NO_3)_3$**, liq. | 2 | 68 | — |
| **$VO(PO_4) \cdot 2H_2O$**, cr.*) | — | — | — [21] |
| **$VO(SO_3F)_3$** cr., red | 120 | dec. 190 | — |
| **$VOF_3$**, cr. | 300 | 480 | −1251 |
| | | subl. > 110 | |
| **$VOCl_3$**, liq., $d$ = 1.829 | −77 | 128 | −740 |
| **$VOBr_3$**, liq. | | 130/vac. | — |
| | | dec. 180 | |
| **$VOCl_2(N_3)$**, $\xrightarrow{t}$ VON + $N_2$ + $Cl_2$ | — | — | — |
| **$VOHal_2(OR)$**, liq. | — | — | — |
| **$VOHal(OR)_2$**, liq. | — | — | — |
| **$VO(OR)_3$**, cr. (R = Me) or liq. (R = Et to $C_5H_{11}$). $\mu$ = 1.1 – 1.2 | | | |

* stab., sol. in $H_2O \approx 1\%$ (viol. soln.)

$VOF_3$ struct.: network of [$VOFF_{4/2}$] octahedra, V = O 1.57, V — F 1.70 (termnl.), 1.8 – 2.3 (br.); $VOHal_3$ (Hal = Cl – Br) in struct. and g.: tetrahedral mols., V = O 1.56, V — Cl 2.12, ∠ClVCl 111 [20]

$ClN_3$

**M[$VOF_4$]**, cr., yel.-grn., struct.: chains of [$VF_5O_{ax.}$] octahedron, V shifted to O by 0.31 from equ. plane, V = O 1.57, V — F 1.79 (equ.), 2.33 (ax.) [23]
**$M_2[VOF_5]$; $Cs_3(VO)_2F_9$**
**[PyH][$VOCl_4$]; $M_2[VOCl_5]$**, M = K – Cs, $NH_4$, grn. [32]

$S_2Cl_2$

$SO_3$ ($SO_2Cl_2$)

$SOCl_2$; C + $Cl_2$;
HCl + $P_2O_5$; $N_2O_5$ — $V_2O_5$

**$V_2O(SO_4)_4$**, yel., unstab.

| | $\Delta H$ | V — Hal |
|---|---|---|
| **$VF_4$**, cr., hyg., yel.-brn., $\xrightarrow{300°}$ $VF_3 + VF_5$↑, in struct.: octahedra layers, | −1412 | 1.69 / 1.92 |
| **$VCl_4$**, liq., red, v. hyg., m.p. ⩽ −20, b.p. 154, slowly dec. 20 (⟶ $VCl_3 + Cl_2$↑) | −694 | 2.14 |
| **$VBr_4$**, cr., red (is formed on cooling the gas (550° ⟶ −78°), dec. −23 (⟶ $VBr_3 + Br_2$), mol.: tetrahedron [46] | −393 | 2.28 |

KCl + ICl

**$M_2VF_6$**, anion: octahedron, V — F 1.61 – 2.29 [16]
**$M_2VCl_6$**, M = K (brn.), Rb (pink), Cs (viol.)
**M[$VCl_5$]**, M = [$PCl_4$], (previously "$VCl_5$", cr., brn., m.p. 260 [17]), [$SCl_3$] (cr., blk., m.p. 32)

$Cl_2$(200°) — V — $F_2$; $BrF_3$

**$VF_5$**, cr., colrl., v. hyg., m.p. 19, b.p. 48, $\Delta H = 1473$, liq. ⇆ $VF_4^+ + VF_6^-$; struct. analogue of $CrF_5$; in g.: mol., trig. bipyr., V — F 1.71 (equ.), 1.73 (ax.); + $H_2O$ ⟶ $V_2O_5$↓ + HF (vigorously); **$[VF_4]^+[SbF_6]^-$** [38]

$VCl_3$ — MCl + $BrF_3$
$MVF_4$ — $XeF_2$

**M[$VF_6$]**, M = $NH_4$, K (dec. 330), Ag, [NO], [$NO_2$], [$Xe_2F_{11}$], cr., colrl.
↓ $H_2O$
**$Ag[VF_4(OH)_2]$** -*trans* [33]

**$VCl(NH_2)_3$**, brn.-grn.
**$VCl_4(NO)$**
**$V_2Cl_7(NO)$, $V_2Cl_8(NO)_5$**, cr., subl.
↓ ROH
**$VCl_2(OR)_2 \cdot ROH$**
**$V(OR)_4$**, cr. or liq., brn., sol. in eth., bz., mol.: tetrahedron [13]
↑ ROH
**$V(NR_2)_4$**
**$V(S_2)_2$**, patronite
**$(C_5H_5)_2VCl_2$**

NaOR

$(VO)^{2+}$ — $OH^- + S^{2-}$

**Thiovanadates (IV)**, sol. in $H_2O$, + $H^+$ ⟶ VS↓ + S + …
**$BaVS_3$**, struct.: linear chains of [$VS_4$] tetrahedra, V — V 2.81, conductor

VN — $Cl_2$(130°)
$VCl_4$ — $HalN_3$

**$Cl_3V = NCl$**, m.p. 132, subl., in gas: monomers (V = N 1.65, N — Cl 1.60, V — Cl 2.14, ∠ClVCl 113, ∠VNCl 170), [14] in struct.: dimers with 2 Cl (br.)
**$Cl_3V = NHal$**, Hal = Br, I, mol.: trig. pyr. (NHal – ax.)

**$M_2[V(CN)_7]$**, CN V = 7

**M[$VO_2S$] · $H_2O$; $Na[VOS_2] \cdot 2H_2O$**

**$V_2S_5$**↓, powder, brn., sol. in alk., $M_2S$, dil. $HNO_3$, is readily oxidised in air, $\xrightarrow{t}$ $V(S_2)_2 + V_2S_3$ + …

$M_2S$ ⇄ 60° ($N_2$)

**$(NH_4)_3[VS_4]$**, thiovadanate, cr., viol. (soln. – cherry-red), anion: tetrahedron, V — S 2.15

$NH_4VO_3$ — $(NH_4)_2S$