VANADIUM

V ions in aqueous solutions, see p. 52

References

V^0 — 3d: ↓ ↓ ↓ | 4s: ↓↑ | 4p: | **E.N.** 1.5

$V_2O_5 + Fe_2O_3$ —(C; Si; Al)→ **Ferrovanadium**
30–80% V; 3.5% Si; >2% Al; 1% C; 0.1–0.2% P and S; 70–10% Fe. A subtraction solid soln. and **VFe** (m.p. 1234) occur in the Fe–V system.

Vanadium steels
(0.2% V) ductile, tensile, high abrasion resistance and rupture strength.
Al–V alloys corrosion-resisting

V_2O_5 —(Al; Fe; Ca)→ **V**, met., wh., solid, $d = 6.1$, m.p. 1920, b.p. 3450, $E_0 V^{2+}/V_s = -1.17$; $E_0 V^{3+}/V_s = -0.86$; sol. in HF, aq. reg. (20°), HNO_3, H_2SO_4 – conc. (t); α-Fe type cub. struct., $a = 3.03$, V—V 2.68

V —(M)→ Ferrovanadium

V —(Hal_2)→ **V_3S**

V —(Br_2; I_2)→ **VCl_3**

V_8O; V_4O; $V_2O_{1\pm x}$ [41]

$VO_{1\pm n}$, $n = 0.25$, cr., blk. with met. lustre, m.p. 1830, $\Delta H = -412$, sol. in ac., conductor (at high t – semiconductor), NaCl type struct., V—O 2.05, V—V 2.89 [5]

$V(OH)_2$↓, brn., sol. in ac.

$V(ClO_4)_2 \cdot 6H_2O$, needles, red-viol.

$VSO_4 \cdot nH_2O$, $n = 7$ (viol. vitriol, isostruct. to $FeSO_4 \cdot 7H_2O$), 6, 4, 1
· **$M_2SO_4 \cdot 6H_2O$**, Tutton's salts

$[V(H_2O)_6](CF_3SO_3)_2$, V—O 2.12 [3]

2+ (d^3)

3+ (d^2)

V_2O_3, cr., blk., m.p. 1970, $\Delta H = -1239$, sol. in ac., karelianite, corundum (Al_2O_3) type struct., V—O 2.00 —(H_2; C; CO)→ $VO_{1\pm n}$

V_2O_3 —(V (1200°))→ $VO_{1\pm n}$

V_2O_3 —(t ($-H_2O$))→ **VO(OH)**, montroseite, struct. analogue of diaspore (AlOOH)
$V(OH)_3$↓, cr., brn.-grn., sol. in ac., strong Red agent

VO(OH) —(cath. Red)→ NH_4VO_3

V_2O_3 —(MO ($h\nu$, laser))→ 2.8 + **$M^{II}V_{10}O_{15}$**, struct.: network of V^{II}, V^{III} octahedra [39]

MVO_2, M = Li–K, blk., isostruct. to $KFeO_2$ [7]

$M_3[VOCl_4]$, M = K–Cs [9]

V(OH)(SO₄) [2]
$V_2(SO_4)_3$↓, cr., orange (monocl.), grn. (hex.), —400°→ SO_2 + $VOSO_4$ [2]
↑ $-H_2O$
· **nH_2O**, $n = 2, 4, 10$
· **$M_2SO_4 \cdot 24H_2O$**, M = NH_4, Rb, Cs, Tl, viol. alum, stab. in air
$V(H_2PO_3)_3$↓, yel.-grn. [26]

V_2O_5 —($H_2SO_4 + S$)→ **V(OH)(SO₄)**

V_2O_5 —(H_3PO_4)→ **VPO₄**, brn.
↑ H_3PO_4
$[V(PO_3)_3]_n$, $n = 4, \infty$; yel.-grn., struct.: chains of $[VO_6]$ octahedra and $[PO_4]$ tetrahedra, P—O 1.98
$V_4(P_2O_7)_3$, struct.: pairs of $[V_2O_9]$ octahedra, V—O 1.8–2.2
$V(CH_3COO)_3$
$[V_3O(CH_2ClCOO)_6(H_2O)_3]^+X^- \cdot 3H_2O$, struct. analogue of Cr (III) acetate [2]

$H[V(SO_4)_2] \cdot nH_2O$, $n = 4, 6$, cr., grn. [8] —(230°)→ **V(OH)(SO₄)**

$M[V(SO_4)_2]$, cr., grn., · **$6H_2O$**, viol., struct.: $[VO_6]$ octahedra, V—O ~1.98 [26]
$Na_3V(SO_4)_3$
$Cs[VHP_3O_{10}]$, $Rb[V(HPO_4)_2]$
$Cs[V_2P_5O_{16}]$, struct.: chains of $[PO_4]$ tetrahedra combined with $[VO_6]$ octahedra, V—O 1.91–2.06

$M_3[V(C_2O_4)_3]$, anion: octahedron [26]

$M_3[V(C_2O_4)_3]$ —($V + H_3PO_4$; SO_2 ($NaHSO_4$))→ V_2O_5

VOF
VOCl, powder, brn.
VOBr, cr., viol., dec. 480
VOI, stab. < VOBr < VOCl [37]

0 (d^5)

$HV(CO)_6$, unstab. [1]
↑ H^+
$M[V(CO)_6]$, M = Na, K, NH_4, $[R_4N]$, cr., yel., stab., diamagn., anion: octahedron, $\Sigma e = 18$
↓ PR_3 ($h\nu$-UV)
$M[V(CO)_4(PR_3)_2]$
$[R_4N][V(CO)_5(PR_3)]$
$M_3V(CO)_5$

$HV(CO)_6$ —(M)→ **$M_3V(CO)_5$**

$HV(CO)_6$ —(Na; H_3PO_4)→ **$V(CO)_6$**

$V(CO)_6$, cr., blue-grn., subl. 40–50 vac., dec. 60, Ox in air, orange solns. in org. solvs. v. unstab.; paramagn. ($\Sigma e = 17$!), mol.: distort. octahedron, V—C 2.01, C—O 1.14 [35]

$V(CO)_6$ —(CO + Mg/Zn (Py, 1, p))→ **VCl_3**

$[V(Thf)_4]^{2+}[V(CO)_6]_2^-$, mol.: chain of 3 octahedra [35]

$V(:CO)_5(:NO)$, stab. > > $V(CO)_6$, ($\Sigma e = 18$)
$(R_3P)Au–V(CO)_6$

$[V(CO)_5(PR_3)]$, cr., grn., m.p. 104 [35]
$V[(—CH_2—PR_2)_2]_3$

$[VDipy_3]$, octahedron mol.
$[V(C_6H_4F_2 - 1.4)_2]$, mol.: sandwich
$V(C_6H_6)_2$, dibenzenevanadium

$[VDipy_3]^+X^-$, cation: octahedron

Li[VDipy₃] · 4 Thf

$K_5[V(CN)_5(NO)^+]$

$K_5[V(CN)_5]$, cr., pink

V_3S

VS_{1+n}↓, $n = 0.17–0.53$, powder, blk., sol. in H_2SO_4 (t), M_2S, NiAs type struct.
V_3S_4 and **V_5S_8**, distort. struct. NiAs type, V—V ≈ 2.9; **V_2S_3** [43]

VF_2, cr., light-grn., CaF_2 type struct.; · **$4H_2O$**, blue-viol. — ΔH —
VCl_2, cr., light-grn., m.p. 1350, subl. 1000, CdI_2 type struct.; · **$4H_2O$** — −451
VBr_2, cr., brn., CdI_2 type struct.; · **$6H_2O$** — −348
VI_2, α-cr., blk., subl. 800, β-, red, CdI_2 type struct.; —>1400°→ V + I_2, $\mu_{eff} \approx 3$ — −264
$VHal_2 \cdot nNH_3$; **$VHal_2 \cdot nL$**, L = Thf, C_6H_5OH, **$[V(\mu\text{-}Cl)_3Thf_6]^+X^-$** [45]

VCl_3 —(HF)→ **VF_2**, **VCl_2**
VCl_3 —(ex.)→ **VBr_2**, **VI_2**
VCl_3 —(deficiency)→ **VI_2**

VF_2 —(t ($-Hal_2$); H_2 (t))→ **VF_3**, **VCl_3**, **VBr_3**, **VI_3**

MVF_3, M = Na–Rb
$MVCl_3$, M = K (m. p. 946), NH_4, Tl
K_2VCl_4
$Cs_2VCl_4 \cdot 2H_2O$
$MVBr_3$, pink-brn.
$KVBr_3 \cdot 6H_2O$, viol. [4]

$K_4[V(CN)_6] \cdot 3H_2O$, yel., anion: octahedron V—C 2.16, C—N 1.15, $\mu_{eff} = 3.83$
$K_4[V(CN)_6(NO)]$, diamagn.
$M_4[V(NCS)_6] \cdot nH_2O$, $\mu_{eff} = 3.8$ [40]

$V(C_5H_5)_2$, vanadocene, cr., viol., m.p. 173, sol. in eth. and C_nH_m, Ox in air, paramagn. (3 unpaired e), struct. analogue of ferrocene, V—C 2.28, C—C 1.43 [36]

$V(C_5H_5)(CO)_4$, cr., yel., m.p. 138, diamagn. —(CO)→ **$V(C_5H_5)_2$**

$V(C_5H_5)_2$ —(V_2O_5; NH_4F ($-N_2$))→ **VF_3**

VF_3, cr., grn., subl. 800, isostruct. to $FeCl_3$ [18] — ΔH −1335 — · **$3H_2O$**
VCl_3, cr., viol., nonvolatile, —500°→ VCl_2 + VCl_4, isostruct. to $FeCl_3$ — −782 — · **$6H_2O$**
VBr_3, blk.-grn., —280°→ VBr_2 + Br_2, isostruct. to $FeCl_3$ — −452
VI_3, blk., —280°→ VI_2 + I_2, isostruct. to BiI_3; $\mu_{eff} = 2.92$ [3] — −280
All $VHal_3$ weakly hyg., poorly sol. in H_2O, better sol. in alc.; in struct. $VCl_3 \cdot 6H_2O$: cation $[VCl_2(H_2O)_4]^+$
trans-**$[VCl_3(SMe_2)_2]$**, mol.: trig. bipyr.

K_3VF_6, m.p. 1020, V—F 1.93 [25]
$(NH_4)_3VF_6$↓, m.p. 1400, yel.-grn.
$M_2[VF_5(H_2O)]$, cr., grn.
$M[VF_4(H_2O)_2]$
$M[VCl_4]$, anion: tetrahedron, · **nH_2O**, M = K–Cs, $n = 0$ (viol.), 1 (red), 4 (grn.)
$Cs_2[VCl_2(H_2O)_4]Cl_3$-*trans*; **$Cs_3[VCl_2(H_2O)_4]Cl_4$**, V—O 1.97, V—Cl 2.37
M_2VCl_5, M_3VCl_6, $M_3[V_2Cl_9]$, anions: trig. bipyr., octahedron, pairs of octahedra with common edges, V—Cl 2.17–2.44
$M[VBr_4]$, **$Cs_2[VBr_2(H_2O)_4]Br_3$**-*trans*

VF_3 —(t ($-Cl_2$))→ **K_3VF_6**

$[V(NH_2)(NH_3)_5]Hal_2$ (earlier "$VHal_3 \cdot 6NH_3$"), red
$V(NH_2)Cl_2$ —300°→ **V(NH)Cl** —t→ **VN**
$VCl_2(OMe)$, cr., grn.
$VCl(OMe)_2$ [6]
$V(OR)_3$, cr., grn., hyg., insol. in alc., nonvolatile

$K_3[V(CN)_6] \cdot 3H_2O$, cr., red
$K_4[V(CN)_7] \cdot 2H_2O$, viol., anion: pentag. bipyr., V—C 2.15
$M_3[V(NCS)_6]$, M = Na (· $12H_2O$), K [10]

$[V(C_5H_5)_2]^+X^-$, vanadocene salts, red

Li[VS_2] [11] —($Li_2CO_3 + H_2S$ (500°))→ V_2O_5

VN, **V_3N** **Li_7VN_4** **VP**, **VP_2**, **V_3P_2**, **V_2P**, **V_3P**	**VC_2**, $+ H_2O \rightarrow C_2H_4 + C_2H_2 + \cdots$ **VC**, m.p. 2830, NaCl type struct. **V_2C**, hex. close pack **V_3Si**	**VB_2**, **V_3B_4**
metal-like interstitial phases in the struct. of V		