The O-V (Oxygen-Vanadium) System*

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Equilibrium Diagram

The equilibrium solid phases of the V-O system at 0.1 MPa hydrostatic pressure are (1) the bcc terminal solid solution, (V); (2) bct α'; (3) bct β; (4) bct β'; (5) monoclinic γ; (6) fcc δ; (7) bct δ'; (8) V_2O_3, with rhombohedral and monoclinic forms above and below -112 °C; (9) V_3O_5, with different monoclinic forms above and below +155 °C; (10) the triclinic V_nO_{2n-1} Magnéli series, with n = 4, 5, 6, 7, and 8; (11) VO_2, with tetragonal β and monoclinic α forms above and below + 68 °C; (12) V_6O_{13}, with different monoclinic forms above and below -124 °C; (13) monoclinic V_3O_7; and (14) orthorhombic V_2O_5. Numerous alternative designations to those adopted occur in the literature. Most solid phases exhibit detectable composition ranges, except for V_3O_5, the Magnéli phases, V_6O_{13}, and V_3O_7, where the breadths are on the order of the experimental uncertainties. The ranges in VO_2 and V_2O_5 are also very narrow. Among the many other phases reported, most are either unconfirmed or demonstrably unstable. The established phases V_9O_{17} and V_4O_9 might be marginally stable, but they are omitted from the assessed V-O phase diagram (Fig. 1).

The pioneer draftings of the V-O phase diagram—[53Sey] and [57Bur] below and above 60 at.% O, respectively—incorporated both long-known and then recently discovered phases: (V), β, δ, V_2O_3, V_3O_5, V_nO_{2n-1} Magnéli, VO_2, V_6O_{13}, and V_2O_5. Major revisions followed. Phases were deleted ("γ" of [53Sey]) or added by [55Ros] (γ), by [66Tod] (V_3O_7, discovered by [65Tud]), by [70Hen] (α', discovered by [69Cam]), by [71Bel] (δ', discovered by [42Kle]), and by [74Hir] (β', discovered by [73Hir]). The phase relationships and invariant equilibria depicted in the assessed diagram (Fig. 1), which incorporates all of these phases, were derived primarily below 55 at.% O from the diagram of [71Ale] (modified by detail from [71Bel] and [75Hir2]) and above 67 at.% O from [66Tod] (modified by detail from [80Vas]). Between 55 and 67 at.% O, the main influence was the [66Kac] diagram. Table 1 lists the known phase transformations and invariant equilibria.

*Unabridged version of this assessment can be found in *Phase Diagrams of Binary Vanadium Alloys*, Monograph Series on Alloy Phase Diagrams, by J.F. Smith, published by ASM INTERNATIONAL, July 1989.

Fig. 1 Assessed V-O Phase Diagram (Condensed System, 0.1 MPa)

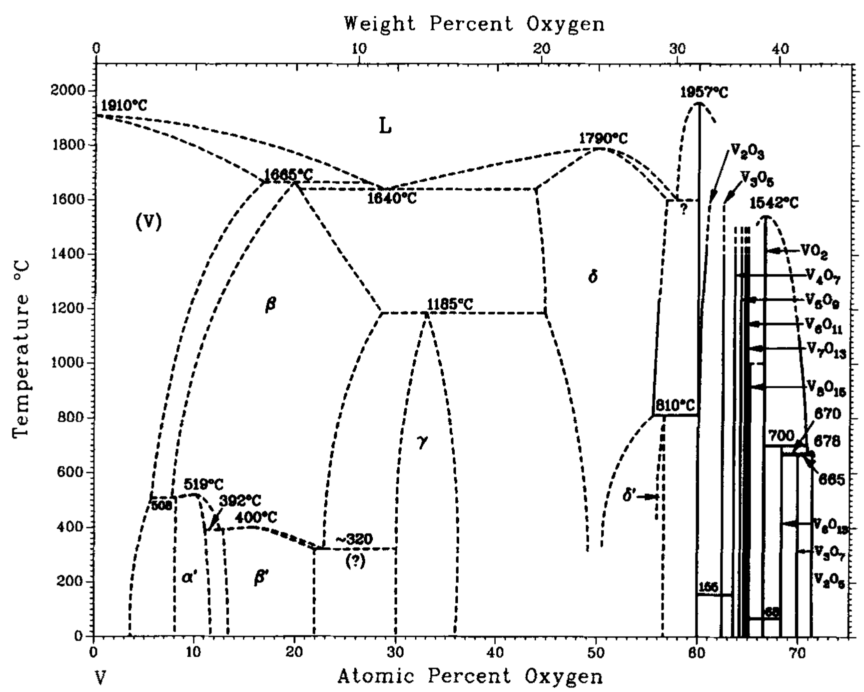

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Table 1 Special Points of the Assessed V-O Phase Diagram (Condensed System, 0.1 MPa)

Reaction	Composition of the Respective phases, at.% O			Temperature, °C	Reaction type
L ↔ V		0		1910	Melting point
L ↔ δ		~50		1790	Congruent
L ↔ h-V_2O_3		60		1957	Congruent(?)
L ↔ V_nO_{2n-1}(a)		...		...	Incongruent(?)
L ↔ βVO_2		66.7		1542	Congruent
L ↔ V_2O_5		71.4		678	Congruent
β ↔ α′		10		519	Ordering
β ↔ β′		16		~400	Ordering
h-V_2O_3 ↔ l-V_2O_3		60.0		~−112	Polymorphic
h-V_3O_5 ↔ l-V_3O_5		62.5		~155	Polymorphic
βVO_2 ↔ αVO_2(b)		66.7		68	Polymorphic
h-V_6O_{13} ↔ l-V_6O_{13}		68.4		−124	Polymorphic
L + (V) ↔ β	27	17	20	1665	Peritectic
L ↔ β + δ	29	20.5	~44	1640	Eutectic
L ↔ δ + h-V_2O_3(c)	~58	~57	~60	~1600	Eutectic
L + V_nO_{2n-1} ↔ $V_{n\pm a}O_{2(n\pm a)-1}$(a)	...	...	...	...	Peritectic
L ↔ V_nO_{2n-1} + $V_{n+a}O_{2(n+a)-1}$(a)	...	...	...	...	Eutectic
L + βVO_2 ↔ h-V_6O_{13}	71.2	~67	68.4	~700	Peritectic
L ↔ h-V_6O_{13} + V_2O_5	71.3	68.4	71.4	~670	Eutectic
β ↔ (V) + α′	8.0	5.9	8.3	508	Eutectoid
β ↔ α′ + β′	12.7	11.0	13.0	392	Eutectoid
β ↔ β′ + γ(c)	~23	~22	30	~320	Eutectoid
β + δ ↔ γ	28.6	~45	33.3	1185	Peritectoid
δ + h-V_2O_3 ↔ δ′	56	60	57	810	Peritectoid
$V_{n-a}O_{2(n-a)-1}$ + $V_{n+b}O_{2(n+b)-1}$ ↔ V_nO_{2n-1}(a)	...	...	...	...	Peritectoid
V_nO_{2n-1} ↔ $V_{n-a}O_{2(n-a)-1}$ + $V_{n+b}O_{2(n+b)-1}$(a)	...	...	...	...	Eutectoid
h-V_6O_{13} + V_2O_5 ↔ V_3O_7	68.4	71.4	70	~665	Peritectoid
h-V_2O_3 + 1–V_2O_3 + δ′(c)	60	60	57	~−112	Unknown
h-V_2O_3 + l-V_2O_3 + l-V_3O_5(c)	60	60	62.5	~−112	Unknown
h-V_3O_5 + l-V_3O_5 + h-V_2O_3(c)	62.5	62.5	60	~155	Unknown
h-V_3O_5 + l-V_3O_5 + V_4O_7(c)	62.5	62.5	63.3	~155	Unknown
βVO_2 + αVO_2 + V_8O_{15}(?)(c)	66.7	66.7	65.2(?)	~68	Unknown
βVO_2 + αVO_2 + h-V_6O_{13}(c)	66.7	66.7	68.4	~68	Unknown
h-V_6O_{13} + l-V_6O_{13} + αVO_2(c)	68.4	68.4	66.7	~−124	Unknown
h-V_6O_{13} + l-V_6O_{13} + V_3O_7(c)	68.4	68.4	70	~−124	Unknown

(**a**) Where $n = 2$ to 8 (or 9); a and b are positive integers, which may be unity. The number and types of reactions involving each of V_3O_5 and the Magnéli phases are not established. Few of the listed reactions, if any, have been observed. (**b**) For $VO_{2.000}$. (**c**) Required or probable, but not reported as observed.

For the location of solid-phase boundaries in Fig. 1, data from many specialized sources were used; however, as dashed lines in Fig. 1 indicate, several locations remain questionable. Arranged chronologically for each phase, the most important of these sources were (V) [70Hen, 71Ale, 75Fro, 75Hir2, 76Ste], α′ [70Hen, 71Ale, 75Hir2], β [71Ale, 75Hir2], β′ [75Hir2], γ [63Wes, 82Vas], δ [55Ros, 59Vol, 71Ale, 74Wat, 76Vas, 81Arb], δ′ [71Bel], V_2O_3 [67Kat, 70Wak, 77Opp], V_3O_5 [77Opp], Magnéli V_nO_{2n-1} [70And1, 77Opp], VO_2 [75Opp2], V_6O_{13} [75Opp1], and V_2O_5 [66Tod, 77Dzi, 77Opp]. The liquidus branches were located to pass through the melting points of V [Melt], δ [71Ale], V_2O_3 [73Sly], VO_2 [75Opp1], and V_2O_5 [86Fer], as well as the (V) + β + L peritectic and β + L + δ eutectic points [71Ale]. Apart from portions near the latter pair of invariants [71Ale] and on the VO_2 liquidus [71Sui, 75Opp1], most of the liquidus curves as drawn are speculative. Incongruent melting of V_3O_5, the Magnéli phases, and VO_2 was suggested [65Roy, 70And1], but experimental evidence is lacking.

Crystal Structures and Lattice Parameters

The crystal structures and lattice parameters of the stable phases are listed in Tables 2 and 3, respectively, together with those of nonequilibrium phases for which such data are available. Transitions involving electrical and/or magnetic properties, some of technical importance, occur also without crystallographic change in V_3O_5, the Magnéli phases, and possibly V_2O_5 [64Hae, 73Kac]. The crystal structures of most stable phases are firmly established, but consensus on γ and δ′ appears to be lacking.

Table 2 V-O Crystal Structure Data

Phase	Composition, at.% O	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
Stable phases						
(V)	0 to 17	$cI2$	$Im\bar{3}m$	$A2$	W	[King1]
α'	8.1 to 11.7	$tI216$(a)	...	...	...	[75Hir2]
β	7.9 to 28.5	$tI2.5$(b)	$I4/mmm$	...	...	[71Ale]
β'	13 to 22	$tI76$(c)	$I4/mmm$	...	$V_{16}O_3$	[73Hir]
γ	30 to 35	$mC20$(d)	$C2/m$	...	$V_{14}O_6$	[75Hir1]
δ	42 to 57	$cF8$	$Fm\bar{3}m$	$B1$	NaCl	[70Ban]
δ'	54 to 56	$tI116$	$I4_1/amd$	...	$V_{52}O_{64}$	[70And2]
l-V_2O_3(e)	~60	$mI20$	$I2a$	...	...	[70Mcw]
h-V_2O_3(f)	60.0 to 60.5	$hR10$	$R\bar{3}c$	$D5_1$	αAl_2O_3	[28Zac]
l-V_3O_5(e)	62.49 to 62.52	$mP32$	$P2/c$	...	V_3O_5	[80Asb]
h-V_3O_5(f)	~62.5	$mI32$	$I2/c$	...	...	[82Hon]
V_4O_7	63.6	$aP22$	$P\bar{1}$	...	V_4O_7	[Pearson3]
V_5O_9	64.3	$aP28$	$P\bar{1}$	...	V_5O_9	[Pearson3]
V_6O_{11}	64.7	$aP34$	$P\bar{1}$	...	V_6O_{11}	[Pearson3
V_7O_{13}	65.0	$aP40$	$P\bar{1}$	...	V_7O_{13}	[Pearson3]
V_8O_{15}	65.2	$aP46$	$P\bar{1}$	...	V_8O_{15}	[78Gan]
αVO_2(e)	66.7	$mP12$	$P2_1/c$	...	VO_2	[Pearson3]
βVO_2(f)	66.6 to 66.9	$tP6$	$P4_2/mnm$	$C4$	TiO_2 (rutile)	[Pearson3]
l-V_6O_{13}(e)	~68.4	$mP38$	$P2_1/a$	...	...	[73Kaw]
h-V_6O_{13}(f)	~68.4	$mC38$	$C2/m$	...	V_6O_{13}	[48Aeb]
V_3O_7	~70	$mC120$	$C2/c$	...	V_3O_7	[74Wal]
V_2O_5	~71.4	$oP14$	$Pmnm$	...	V_2O_5	[50Bys]
Other Phases						
Martensite-A	6.7 to 8.6	tI^*(g)	...	$L'2$(?)	Martensite	[70Hen]
Martensite-B	6 to 6.7	tI^*(g)	...	$L'2$(?)	Martensite	[71Ale]
ε	22 to 28	mP^*	$P2_{1/c}$	...	...	[80Arb]
$VO_{1.17}$	~54	...	$I4_{1/a}$	...	...	[70And2]
V_9O_{17}	~65.4	$aP52$	$P1$	...	V_9O_{17}	[81Kuw]
VO_2–B	~66.7	$tI288$(?)	...	...	...	[70Sat]
VO_2-M_2	~66.7	$mC24$	$C2/m$	...	...	[73Cha2]
VO_2–T_2	~66.7	$tP6$	$P4_2/mnm$	$C4$	TiO_2 (rutile)	[73Cha2]
VO_2–M_3	66.8 to 67.2	$mP6$	$P2/m$	...	...	[73Cha2]
VO_2–M_4(h)	~66.7	$mC24$	$C2/m$	...	...	[76The]
VO_2–D	~66.7	$oP12$	$Pbnm$	...	$HA1O_2$ (diaspore)	[74Mul]
V_6O_{13}–C	~68.4	$cP76$(?)	...	...	...	[70Sat]
V_6O_{13}–D	~68.4	$mC38$	$C2/$m	...	...	[68The]
V_4O_9	~69.2	$oP52$	$Pnma$	...	V_4O_9	[70Wil]
V_4O_9–E	~69.2	$oP104$(?)	...	...	V_4O_9	[77Gry]
V_2O_5	~71.5	...	...	...	Glass	[67Ken]

(a) At V_8O. **(b)**At V_4O. **(c)**At $V_{16}O_3$. **(d)**At V_7O_3. **(e)**Below transformation temperature, T_{trs}. **(f)** Above T_{trs}. **(g)**2 atoms V/unit cell. **(h)** Called $VO_2(B)$ by [76The].

Thermodynamics

The thermodynamics of oxygen dissolved in the (V), β, and γ phases were described by [75Fro], [76Ste], and [83Vas], and those of the phases δ, V_2O_3, VO_2, and V_2O_5 were reviewed by [79Smi] and [82Ran]. Calorimetric standard enthalpies of formation are available for V_3O_5, the Magnéli phases, and V_6O_{13} [73Cha1], but the lack of low-temperatures heat capacity values required that entropy values be based on high-temperature equilibrium data [75Vas, 80Vas]. Standard enthalpy of formation and entropy values for V_3O_7 were estimated by [80Vas]. Few reliable data are available explicitly for α', β', and δ'.

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Table 3 V-O Lattice Parameter Data at Room Temperature

Phase	Composition, at.% O	Lattice parameter, nm a	b	c	Comment	Reference
Stable						
(V)	0	0.30238	...	...	At 25 °C	[King1]
α'	8.9	1.2436	...	1.7940	...	[75Hir2]
β	20.0	0.2970	...	0.340	Cell with two V atoms	[71Ale]
β'	15.2	1.196	...	0.6604	...	[73Hir]
γ	30.6	0.9507	0.2935	0.7695	$\beta = 90.84°$	[75Hir1]
δ	50.0	0.4070	...	...	...	[71Reu]
δ'	55.2	1.172	...	0.8245	...	[70And2]
l-V_2O_3(a)	60.0	0.7255	0.5002	0.5548	$\beta = 96.75°$, at −196 °C	[70Mcw]
h-V_2O_3(b)	60.0	0.49515	...	1.4003	...	[70Der]
l-V_3O_5(a)	62.5	0.9859	0.50416	0.6991	$\beta = 109.478°$, at 25 °C	[80Asb]
h-V_3O_5(b)	62.5	0.9846	0.50268	0.7009	$\beta = 109.536°$, at 185 °C	[82Hon]
V_4O_7	63.6	0.5504	0.7007	1.9243	$\alpha = 41.3°, \beta = 72.5°, \gamma = 109.4°$	[76Hor]
V_5O_9	64.3	0.5470	0.7005	2.4669	$\alpha = 41.4°, \beta = 72.5°, \gamma = 109.0°$	[76Hor]
V_6O_{11}	64.7	0.5448	0.6998	3.0063	$\alpha = 41.0°, \beta = 72.5°, \gamma = 108.9°$	[76Hor]
V_7O_{13}	65.0	0.5439	0.7005	3.5516	$\alpha = 40.9°, \beta = 72.6°, \gamma = 109.0°$	[76Hor]
V_8O_{15}	65.2	0.5432	0.6989	3.7078	$\alpha = 98.76°, \beta = 128.39°, \gamma = 108.93°$	[78Gan]
αVO_2(a)	66.7	0.575173	0.452596	0.538326	$\beta = 122.6148°$, at 24.8 °C	[79Kuc]
βVO_2(b)	66.7	0.455358	...	0.284982	At 69.3 °C	[79Kuc]
l-V_6O_{13}(a)	68.4	1.196	0.3713	1.007	$\beta = 100.9°$, at −196 °C	[73Kaw]
h-V_6O_{13}(b)	68.4	1.1922	0.3680	1.0138	$\beta = 100.87°$, at 20 °C	[71Wil]
V_3O_7	70.0	2.1921	0.3679	1.8341	$\beta = 95.61°$, at 20 °C	[74Wal]
V_2O_5	71.4	1.1510	0.4369	0.3563	...	[61Bac]
Other phases						
Martensite-A	6.7	0.3034	...	0.3096	$c/a > 1$, (c)	[70Hen]
Martensite-B	6.7	0.3081	...	0.3003	$c/a < 1$, (c)	[71Ale]
ε	~25	1.668	1.650	1.760	$\beta = 90.3°$	[80Arb]
$VO_{1.17}$	~54	2.608	...	0.803	...	[70And2]
V_9O_{17}	~65.4	0.5418	0.7009	4.5213	$\alpha = 39.3°, \beta = 74.5°, \gamma = 108.9°$	[81Kuw]
VO_2-B	~66.7	1.74	...	0.864	...	[70Sat]
VO_2-M_2	~66.7	0.9083	0.5763	0.4532	$\beta = 91.30°$	[73Cha2]
VO_2-T_2	~66.7	0.4552	...	0.2852	...	[73Cha2]
VO_2-M_3	66.8	0.4506	0.2899	0.4617	$\beta = 91.79°$	[73Cha2]
VO_2-M_4	~66.7	1.203	0.3693	0.642	$\beta = 106.6°$	[76The]
VO_2-D	~66.7	0.4899	0.9446	0.2916	...	[74Mul]
V_6O_{13}-C	~68.4	0.880	...	...	...	[70Sat]
V_6O_{13}-D	~68.4	1.19	0.367	1.01	$\beta = 101°$	[68The]
V_4O_9	~69.2	1.7926	0.3631	0.9396	...	[70Wil]
V_4O_9-E	~69.2	0.8235	1.032	1.647	...	[77Gry]

(a) Below transformation temperature, T_{trs}. **(b)**Above T_{trs}. **(c)**From relationships based on [71Ale] and [70Hen] data.

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#Indicates presence of a phase diagram.

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The Al-Am (Aluminum-Americium) System

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A phase diagram is not available for this system, which was reviewed by [Moffatt]. Two intermediate phases have been verified—$AmAl_2$ by [76Ald] and $AmAl_4$ by [82Con]. Crystal structures for Am-Al phases are listed in Table 1, and lattice parameters are given in Table 2.

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Table 1 Am-Al Crystal Structure Data

Phase	Composition, at.% Al	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
αAm(a)	0	*hP4*	$P6_3/mmc$	*A3'*	αLa	[Massalski]
βAm(b)	0	*cF4*	$Fm\bar{3}m$	*A1*	Cu	[Massalski]
γAm(c)	0	*cI2*	$Im\bar{3}m$	*A2*	W	[Massalski]
$AmAl_2$	66.7	*cF24*	$Fd\bar{3}m$	*C15*	Cu_2Mg	[76Ald]
$AmAl_4$	80	(d)	...	...	...	[82Con]
Al	100	*cF4*	$Fm\bar{3}m$	*A1*	Cu	[Massalski]

(**a**) Up to <769 °C. (**b**) From 769 to <1077 °C. (**c**) From 1077 to 1176 °C. (**d**) Orthorhombic.

Table 2 Am-Al Lattice Parameter Data

Phase	Composition, at.% Al	Lattice parameters, nm *a*	*b*	*c*	Comment	Reference
αAm	0	0.34681	...	1.1241	At 25 °C	[Massalski]
βAm	0	0.4894	...	...	At >769 °C	[Massalski]
γAm	0	...	...	...	At >1074 °C	[Massalski]
$AmAl_2$	66.7	0.7861	...	...	At 21 °C	[76Ald]
$AmAl_4$	80	0.442	0.626	1.366	At 21 °C	[82Con]
Al	100	0.40496	...	...	At 25 °C	[Massalski]

Al-Am evaluation contributed by **M.E. Kassner**, Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA 94550 and **D.E. Peterson**, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No W-7405-ENG-48. Literature searched through mid-1987. Dr. Kassner is the ASM/NIST Data Program Contributing Editor and Dr. Peterson is the ASM/NIST Data Program Category Editor for binary actinide alloys.