The Cd-O (Cadmium-Oxygen) System

112.41   15.9994

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Equilibrium Diagram

The equilibrium solid phases of the condensed Cd-O system at 0.1 MPa hydrostatic pressure are (1) the cph terminal solid solution, (Cd), with a very narrow composition range; (2) the fcc oxide, CdO, with a narrow but significant composition range; and (3) the cubic peroxide, CdO_2, with an unknown composition range. The crystal structures and lattice parameter data are listed in Tables 1 and 2.

No published phase diagram for the Cd-O system was found. A required three-phase equilibrium of the condensed system has not been observed but is listed with other known transformations in Table 3. The melting point of CdO is unknown. CdO_2 has been omitted from Table 3 because the nature and temperature of its transformation(s) are unknown. No polymorphic changes are known for any of the phases at 0.1 MPa hydrostatic pressure. Because the only data for phase boundaries are fragmentary and limited to the Cd-rich liquidus of CdO (liquid Cd compositions) and the corresponding solidus, the phase diagram (Fig.1) has few details.

Terminal Solid Solution, (Cd). This phase is stable only at low fugacities of O_2 (Table 4). In the condensed system, O-saturated (Cd) is in equilibrium with CdO. The (Cd) solvus has not been determined. Although no data are available, the present evaluator concludes, on the basis of

the minute solubility of O determined for liquid Cd, that the (Cd) field is very narrow. The (Cd) solidus and liquidus are also undetermined.

The compositions of O-saturated liquid Cd in equilibrium with CdO were determined indirectly by [81Ots], who used electrochemical cells to determine the standard Gibbs energy changes for solution of gaseous O_2 in liquid Cd at 500 °C and for formation of CdO from liquid Cd and gaseous O_2 at 469 to 558 °C. The equation established by [81Ots] for the saturated liquid Cd compositions is

$$\ln C = 11.73 - 14\,309/T$$

where C and T are in at.% O and K, respectively.

O concentrations, including extrapolated values, that were calculated with this equation (and which are, thus, points on the Cd-rich liquidus of CdO) are listed in Table 5. There are no other determinations.

Cadmium Oxide, CdO. This phase exhibits no solid-state transformations. The only attempt to determine the melting point was unsuccessful because the specimen sublimed above 1500 °C without melting [61Rot].

At its Cd-rich limit CdO is in equilibrium with (Cd) or liquid Cd. Although the equilibrium has not been realized, it appears that CdO would be in equilibrium with CdO_2 or

Table 1   Cd-O Crystal Structure Data

Phase	Composition, at.% O	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
Cd(a)	~0	$hP2$	$P6_3/mmc$	$A3$	Mg	[King1]
CdO	49.8 to 50.0	$cF8$	$Fm3m$	$B1$	ClNa	[Pearson2]
CdO_2	~66.7	$cP12$	$Pa3$	$C2$	FeS_2(pyrite)	[Pearson2]

(a) At 25 °C and hydrostatic pressure >13.5 GPa, Cd transforms from cph to double cph. Details unreported [66Per].

Table 2   Cd-O Lattice Parameter Data

| Phase	Composition, at.% O	Temperature, °C	Lattice parameters, nm		Reference
			a	c	
Cd	0	25	0.29788	0.56167	[King1]
CdO	50.0	25	0.46951	···	[Landolt]
CdO_2(a)	~66.7	RT	0.5311	···	[79Kje]

(a) Slightly impure.

Table 3   Special Points of the Assessed Cd-O Phase Diagram (Condensed System)

Reaction	Compositions of the respective phases, at.% O			Temperature, °C	Reaction type
(Cd)–L–CdO(a)	~0	$\sim4 \times 10^{-6}$	~49.9	~321	Unknown
L ⇌ Cd		0		321.108	Melting point
L ⇌ CdO(b)		~50		>1500	Melting point(c)

Note: At 0.1 MPa.
(a) No investigation reported. (b) Not observed because of sublimation. (c) Congruency not established.

Fig. 1 Assessed Cd-O Phase Diagram (Condensed System)
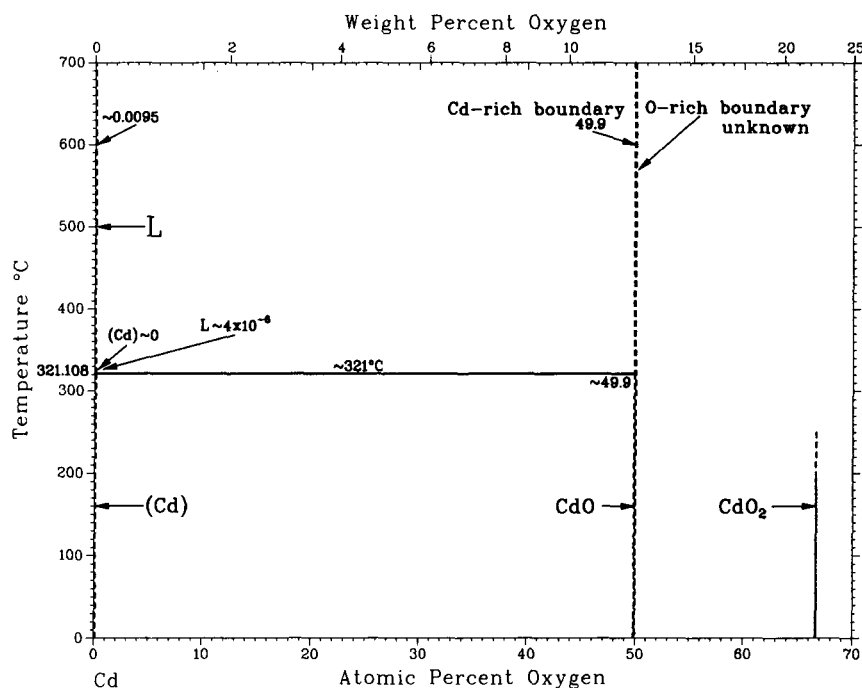
H.A. Wriedt, 1987.

liquid at its O-rich limit, if sufficiently high O_2 fugacities were imposed. The range of compositions of CdO is fairly narrow, but the variation is technically important because of the large change in electrical conductivity that attends the change in the O content [33Bau].

Very little research has been directed at determining the boundary compositions; the upper boundaries are completely unknown. No experiments with O_2 fugacities exceeding about 0.1 MPa have been reported, although the upper boundary is at higher fugacities. No specimen of CdO has been shown by chemical (or other) analysis to contain more than the stoichiometric proportion of O_2, but at least a very slight excess of Cd was present in all specimens observed, even those prepared in O_2.

The Cd-rich boundary of CdO was investigated by [44Fai], who annealed CdO with metallic (Cd) in capsules at 320 to 800 °C and determined lattice parameters of the CdO after quenching. These lattice parameters are listed in Table 6, together with compositions calculated therefrom with a calibration based on other data of [44Fai] (see "Crystal Structures and Lattice Parameters"). [72Str] obtained data at 600 and 700 °C, but their absolute lattice-parameter values are not necessarily comparable to those of [44Fai] because the [72Str] value for nearly stoichiometric CdO was greater than the [44Fai] value. Therefore, compositions of Cd-saturated CdO in Table 6 were calculated from the dilations and the derivative of lattice parameter with respect to at.% O from [44Fai]. The deviations from stoichiometry of Cd-saturated CdO at 650 and 700 °C calculated with the [44Fai] data are more than twice those calculated with the [72Str] data. Both sets agree in indicating that the solubility of Cd in CdO increases with increasing temperature. The evidence is inadequate for choosing the better set of values.

Table 4 Pressures (Fugacities) of O_2 Gas at Stable Coexistence of O-Saturated (Cd) or Cd(L) and CdO

Temperature, °C	O_2 fugacity, Pa	Temperature, °C	O_2 fugacity, Pa
25	8.9×10^{-76}	426.8	7.5×10^{-24}
26.8	3.2×10^{-75}	526.8	6.0×10^{-19}
126.8	9.1×10^{-53}	626.8	3.7×10^{-15}
226.8	2.5×10^{-39}	726.8	4.0×10^{-12}
321.1(a)	8.2×10^{-31}	766.8(b)	4.4×10^{-11}
326.8	2.3×10^{-30}		

From [82Pan].
(a) Melting point of Cd.   (b) Boiling point of Cd (101 325 Pa).

Table 5 O Concentrations in Cd(L) in Equilibrium with CdO(s)

Temperature, °C	Composition, 10^4 (at.% O)
321	0.043
350	0.13
400	0.73
450	3.2
500	11
550	35
600	95

[81Ots] equation extrapolated.

Cadmium Peroxide, CdO_2. In no instance has CdO_2 been equilibrated with another Cd oxide or gaseous O_2. Nevertheless, it has been included here as an equilibrium phase of the Cd-O system because it is the highest oxide of which

the existence is established. (Cd superoxide, CdO_4, has not been prepared as a discrete phase.) If sufficiently high O_2 fugacities could be imposed, it is probable that O-rich CdO would coexist in equilibrium with Cd-rich CdO_2.

Although the existence of CdO_2 is widely acknowledged, it probably has not been produced in the pure state [62Van]. In most instances, compounds termed "peroxide" were produced in the presence of water and were either hydrated or contained hydrogen otherwise associated [11Tel, 29Per, 56Van, 59Hof]. ([29Per] and [62Van] listed several investigations prior to 1911.) In some instances, compounds were called "peroxide", although the indicated formulas were not CdO_2 but hydrated or nonhydrated CdO_x, where $2 > x > 1$ [11Tel, 29Per, 61Boi, 62Chi]. (More detail is given concerning these compounds in the section "Metastable and Other Phases") [58Vol] contended that the compound $CdO_2(2H_2O)$, called "peroxide" in his differential thermal analysis (DTA) investigation [54Vol], was not a hydrate of a "true" peroxide but a compound intermediate between a peroxide and a peracid.

The specimens of CdO_2 produced by [56Van] and [59Hof] apparently contained the smallest amounts of combined hydrogen of any specimens prepared in aqueous media. [79Kje] claimed to have dehydrated such CdO_2 specimens by low-temperature anneals in air or O_2. Possibly anhydrous CdO_2 was also prepared in a nonaqueous medium by [54Sch]. Thin films of CdO_2, which were identified by electron diffraction, were reported by [68Mic] to have formed on Cd in air at room temperature. A compound identified as CdOO was detected in the condensed products of reacting evaporated Cd atoms with dilute mixtures of O_3 in Ar [80Pro].

The limits of deviation in composition from stoichiometric CdO_2 are unknown. [62Van] indicated that appreciable amounts of superoxide ion can be incorporated in CdO_2, so that the O-rich limit may lie above the stoichiometric composition. The reports of compositions on the Cd-rich side of CdO_2 noted in the foregoing discussion are not persuasive evidence of an extended phase field; these compositions, if actual, may have been of metastable or ternary compounds or of mixtures of CdO_2 and CdO [38Eme].

Gas. CdO is the only condensed phase other than Cd, solid or liquid, for which vaporization has been investigated. The thermodynamics of CdO vaporization are discussed in the appropriate section. Early investigators thought that vapor formed in the congruent vaporization of CdO was composed of CdO molecules, but [51Bre] showed that it was composed almost entirely of monatomic Cd(g) and O_2 molecules. [80Gra] reported that experiments had detected less than 0.1% CdO in the equilibrium vapor over CdO at all temperatures up to 1056 °C. [81Beh] indicated that the molecular ratio CdO/Cd in the vapor increased with increasing temperature. [84Kaz] reported that CdO was 0.004 % of the equilibrium vapor at 1027 °C.

Metastable and Other Phases

Several oxides other than CdO and CdO_2 were reportedly prepared. Some of these were not identified with specific stoichiometric compositions, such as the oxide found on molten Cd by [50Gru]. He thought that it was possibly a lower oxide than CdO. Other "suboxides" that were identified with specific compositions were Cd_4O, Cd_2O, and

Table 6 Room-Temperature Lattice Parameters and Compositions of CdO Equilibrated with O-Saturated (Cd) or Cd(L) and Quenched

Reference	Equilibration temperature, °C	Lattice parameter(a), nm	Composition(b), at.% O
44Fai	320	0.46960	49.907
	420	0.46965	49.895
	510	0.46970	49.884
	600	0.46975	49.872
	700	0.46981	49.859
	750	0.46984	49.852
	800	0.46987	49.845
72Str	650	0.46977	49.941
	700	0.46980	49.934

(a) [44Fai] values corrected from the original assumed to be kX. (b) By the slope of the least-squares line fitted to the data of Table 8, with a values 0.46919 and 0.46951 nm at 50.000 at.% O for [44Fai] and [72Str], respectively.

Cd_3O_2 [62Chi]. No other report of Cd_3O_2 has been found. [26Fer] obtained by decomposing Cd oxalate a substance that had previously been identified with Cd_4O, but his specimen produced no lines in XRD. [34Hol] reviewed and attempted to reproduce the experiments reported between 1890 and 1920 in which Cd_4O and Cd_2O were said to have been formed by decomposition of Cd oxalate and of basic Cd oxalate or hydroxide, respectively. He did not obtain uniform compounds of the compositions Cd_4O or Cd_2O and the substances formed contained free (Cd). [36Hed] also attempted to prepare Cd suboxide but concluded that it was "incapable of existence" as a solid phase. An unidentified component of an electrolytic deposit from a nitrate solution was assumed by [36Kud] to be Cd_2O. [55And] reported that an electron diffraction pattern of Cd_2O was obtained from the product of an electrical discharge with a Cd cathode in air. Overall, the evidence for the existence of any Cd suboxide remains unsatisfactory.

The possible existence of several different oxides other than CdO_2 that were called "peroxides" was mentioned in the section on CdO_2. Often the given compositions are accompanied by a qualification that they occur hydrated or in combination with Cd hydroxide or H_2O_2. The latter compounds are omitted here as nonbinary but the reported compositions of hydrated oxides will be mentioned because of the implication that they may exist in the anhydrous state. In review, [62Chi] lists these so-called "peroxides" as Cd_2O_3, Cd_5O_8, Cd_3O_5, and Cd_4O_7. [38Eme] listed the latter three but considered them to be mixtures of CdO and CdO_2. The "peroxides" were said by [62Chi] to have formed when Cd hydroxide or a Cd salt was treated with H_2O_2 or CdO with O_3 or even air. [11Tel] included the possible compositions $Cd_6O_{11}(3H_2O)$ and $Cd_8O_{13}(5H_2O)$ for compounds that he prepared. The compositions Cd_3O_5 and Cd_3O_5 (xH_2O), respectively, were reportedly produced in the experiments of [61Boi] and of [29Per], who also reported that $Cd_4O_7(2H_2O)$ had been prepared. The variability of the compositions reported by the different investigators and the existence of hydration in most instances leave the situation doubtful as to which, if any, of these compounds can exist as discrete, anhydrous oxides.

Cadmium superoxide, CdO_4, has not been prepared as a discrete phase [62Van]. [62Van], however, indicated that 13% superoxide developed in "Cd peroxide" treated with

Table 7 Lattice Parameter Values for CdO Prepared in Air, O₂, or Other Nonreducing Conditions

Reference	Lattice parameter, nm	Reference	Lattice parameter, nm
[20Dav](a)	0.473(b)	[40Fel](a)	0.46943, 0.46944
[22Sch](a)	0.473	[44Fai](a)	0.46916
[27Gol](a)	0.470	[53Swa]	0.46952
[27Wal](a)	0.4708	[60Cim]	0.469514
[29Bre](a)	0.4692	[62Hou]	0.46952
[29Ful](a)	0.4690	[66Kha]	0.469511
[29Nat](a)	0.4735	[69Sin]	0.46953
[31Ksa](a)	0.46991	[70Had](a)	0.46937
[33Gre](a)	0.4691	[71Str](c)	0.46950
[38Fai](a)	0.46919	[72Str](c)	0.46950
[38Han](a)	0.468	[84Ris](a)	0.46950

Note: At ~0.1 MPa pressure (corrected to 25 °C and nm).
(a) Measured at unspecified RT. (b) Original report was of a half-cell dimension, 2.36 kX. (c) Originally reported average 0.46951 included data for specimens with excess Cd.

moist air at 100 °C. Reaction of Cd(NO₃)₂ with NaO₂ (sodium superoxide) in liquid NH₃ yielded CdO₂, not CdO₄ [54Sch]. [06Man] mentioned Cd superoxide as occurring in smoke of burnt Cd but omitted details.

Molecules of CdO₃ in solid N₂ or Ar were detected by spectroscopic analysis of products of the "matrix" reaction of vaporized Cd with O₃ which had been mixed with N₂ or Ar [80Pro].

Crystal Structures and Lattice Parameters

(Cd). Because the solubility of O in Cd is extremely small, the change of lattice parameter with composition in (Cd) has not been determined. The value of hydrostatic pressure (13.5 GPa) at which the cph structure of pure Cd transforms to dcph (double cph) at 25 °C [66Per] is presumably the value applicable throughout the small range of (Cd) compositions.

CdO. According to [53Swa], the crystal structure of CdO was first determined by [20Dav], who showed that it consists of individual interpenetrating fcc lattices of the Cd and O components and is of the ClNa type. A discontinuity in thermal expansion at 120 to 200 °C reported by [71Str] and [72Str] may be evidence of a transition, although the investigators were not explicit; otherwise, there is no report of a transition in CdO. From an investigation of the changes in the electrical conductivity of CdO with imposed values of O₂ fugacity, [33Bau] were able to show that the composition of CdO could vary significantly. At O₂ fugacities <0.1 MPa and temperatures up to 700 °C, the lattice contained Cd in excess of the stoichiometric amount. There are no data for O₂ fugacities >0.1 MPa.

Table 7 lists lattice parameter values for specimens prepared under conditions that, as far as they are known, would cause the compositions to be nearly stoichiometric. Particularly in some of the early investigations, detailed information on preparation is unavailable, but it is assumed that they were not prepared in the presence of reducing agents, including Cd metal, or by heating in vacuum or other atmospheres with O₂ fugacities far below 0.1 MPa. Recent data for CdO prepared by calcination of CdCO₃ in N₂ gas of uncertain O₂ fugacity [81Beh] were

Table 8 Lattice Parameters of CdO Specimens

Composition(a), at.% O	Lattice parameter(b), nm	Composition(a), at.% O	Lattice parameter(b), nm
49.886	0.46967	49.957	0.46937
49.914	0.46956	50.000	0.46918
49.929	0.46955		

From [44Fai].
(a) Original excess "Cd %" units were interpreted to mean weight percent of nonstoichiometric CdO. (b) Original units were denoted "Å" but were interpreted to mean kX.

omitted, although it had been indicated that excess Cd would precipitate if heated specimens with excess Cd were cooled slowly [44Fai, 71Str, 72Str].

The thermal expansion of CdO was measured by [60Cim], [69Sin], [71Str], and [72Str]. The [60Cim] data, for the range from about 10 to 41 °C, indicated that a increases by 6.34×10^{-6} nm/°C. This coefficient agrees quite well with the equation of [69Sin], describing his measurements from 32 to 732 °C:

$$a = 0.46937 + 6.207 \times 10^{-6}\,T + 6.08 \times 10^{-10}T^2$$
$$+ 1.23 \times 10^{-13}T^3,$$

where a is in nm and T is in °C. Lattice parameters were measured by [71Str] and [72Str] from −233 to +1027 °C. The thermal expansion coefficient decreased below room temperature (RT) to zero at −233 °C. Above 200 °C, [71Str] and [72Str] applied a correction to their experimental values and obtained a constant value, 5.40×10^6 nm/°C, for essentially stoichiometric CdO between 25 and 600 °C. This correction, which was made with data of [44Fai], deducted the contribution to lattice expansion due to the excess Cd incorporated in CdO at elevated temperature.

The effect of hydrostatic pressure on CdO at RT was investigated by [84Ris]. Between 0.025 and 0.2 GPa, the lattice parameter, measured by XRD, decreased to a minimum and then increased as pressure was raised to 2 GPa. No discontinuity attributable to a transition is depicted in the results. Chemical analyses indicated that the Cd/O atomic ratio increased at higher pressures, but the mechanism of O loss or Cd gain was not explained.

The variation of lattice parameter with composition has been measured only by [44Fai]. The XRD measurements were made with (1) nearly stoichiometric CdO prepared by calcination of Cd(OH)₂ and slow cooling of the calcine in a current of O₂; and (2) specimens of this CdO heated in a vacuum to induce the development of Cd excess, then quenched. The Cd excess increased with heating temperature up to about 800 °C, but it decreased above that temperature, possibly because the exterior of the specimen evaporated too quickly for the core to adjust its composition. The lattice parameter-composition data plotted* (partly tabulated) by [44Fai] are presented in Table 8, with units converted. The following equation describes a regression line fitted to the five data sets in Table 8:

$$a = 0.46919 + (4.39 \times 10^{-3})\,(50 - C)$$

*A minor discrepancy between values reported at different places in [44Fai] appears when Tables 7 and 8 are compared.

where a is in nm and C is in at.% O. It should be noted that a indicated by this equation (0.46919 nm) for stoichiometric CdO is rather different from the selected value in Table 2. The slope was applied in calculating compositions of CdO equilibrated with liquid Cd (Table 6) from the CdO lattice parameters that were reported by [44Fai] and [72Str].

The problem of identifying the nature of the defects associated with the nonstoichiometry has been considered repeatedly since [33Bau] posed it. They suggested that the excess Cd was present as interstitial Cd^{2+} ions plus electrons from their measurements of the relationship between electrical conductivity and O_2 fugacity. The view that the excess Cd was located interstitially was shared by [44Fai], [60Cim], and [72Hay]. The electrical properties of CdO were related to the concentration of excess Cd^{2+} ions by [51Hog] and [56Eng], but the lattice location of these ions was not specified. According to [62Hau], who studied lattice diffusion, and to [71Str] and [72Str], who determined density and lattice parameter, O^{2-}-site vacancies accounted for the deviations from stoichiometry. [71Str] and [72Str] considered that the Cd unpaired by O was present as Cd atoms on cation sites; [62Hau] thought that either Cd atoms or Cd^+ ions might be so located. [70Kof] and [71Kof] measured electrical properties but were unable to decide between interstitial Cd^{2+} ions and O^{2-}-site vacancies. [62Lam] proposed that the defects could be "D centres, or paired vacancies with two trapped electrons, together with anion vacancies". Thus, the type of defect manifested by the Cd excess is not yet identified positively.

CdO₂. The concordant XRD investigations of [56Van], who made the first determination, and [59Hof] showed that CdO_2 has a pyrite-type cubic structure. The difference between their lattice parameter values, 0.5273 and 0.5313 nm, respectively, may have been due to the incorporation of different amounts of impurity, including the effects of water present during preparation of the specimens. [79Kje] obtained the value 0.5311 nm with specimens subjected to a dehydrating anneal. No values of the lattice parameter have been reported for bulk CdO_2 prepared in nonaqueous media. The value 0.520 nm was obtained by electron diffraction of thin films [68Mic].

Thermodynamics

There is no information on the activity and solubility of O in (Cd).

[81Ots] measured the activity of O at high dilution in liquid Cd at 500 °C with an electrochemical cell: [O in liquid Cd/ZrO₂ (+Y₂O₃)/Air, Pt]. O concentration was established coulometrically, with O added to initially deoxidized liquid Cd. At 500 °C, for the reaction:

$$0.5 O_2(g) = \underline{O}(\text{dissolved in liquid Cd})$$
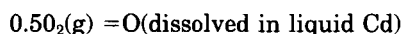
the standard Gibbs energy change is

$$\Delta G^0 = -135.27 \text{ kJ}/0.5 \text{ mol } O_2$$

where the standard state of $O_2(g)$ is at 0.101325 MPa pressure and that of dissolved O is such that activity is equal to concentration (at.%) at infinite dilution. Use of an empirical correlation, which they had developed, allowed [81Ots] to utilize this 500 °C data in expressing the stan-

dard Gibbs energy for this dissolution reaction as a function of temperature:

$$\Delta G^0 = -142\,540 + 9.4\ T$$

where T is in K.

CdO. Nine determinations of the standard enthalpy of formation, $\Delta H_f^0(\text{CdO, 25 °C})$, of CdO were published between 1871 and 1954 and listed by [81Beh]. Omitted was the value -260.9 kJ/mol CdO, obtained calorimetrically by [33Bec]. The value -258.1 kJ/mol CdO, adopted in the compilations of [68Wag], [82Pan], and [84Pan] and in the 1977 CODATA-recommended key values [78Cox], is the mean of emf (-260.0) and calorimetric (-256.1) measurements by [42Mak] and [54Mah], respectively. [81Beh] preferred the [54Mah] value because it was calorimetric, but the [33Bec] value agrees well with that of [42Mak]. The values -259.9 and -259.4 kJ/mol CdO were preferred in the compilations of [62Chi] and [73Bar], respectively. A recent determination by [81Sch] yielded the value -255.7 kJ/mol CdO.

The value for the standard entropy of CdO, $S^0(\text{CdO, 25 °C})$, adopted by [62Chi], [68Wag], [82Pan], [84Pan], and 1977 CODATA [78Cox], is 54.8 J/mol·K, which was presented by [61Kel]. It was based on the S^0 value and the underlying low-temperature heat-capacity data of [28Mil], which apparently are still the only such data for CdO. The value is consistent with the $S^0(25 \text{ °C})$ values for Cd and O_2 and the $\Delta S_f^0(\text{CdO, 25 °C})$ value -23.78 J/mol·K reported by [42Mak]. Recently [81Sch] reported a slightly higher value, 56.6 J/mol·K, for $S^0(\text{CdO, 25 °C})$.

High-temperature enthalpy increments for CdO were measured by [65Mez] (25 to 701 °C) and [72Mil] (25 to 1177 °C); the latter also reported heat capacities and entropy increments to 1227 °C. The CODATA values for ΔH_f^0 (25 °C) and S^0 (25 °C), together with the data of [72Mil], were the basis for the comprehensive tables of thermodynamic properties for CdO(s) up to 1227 °C published by [82Pan] and, in shorter form, by [84Pan].

Early reports of measurements of the vapor pressure of CdO by [29Fei] (weight loss in a stagnant atmosphere), [33Hin] (entrainment), and [41Uye] (weight loss in effusion) indicated that the vaporization process was congruent and by evaporation of CdO molecules. [51Bre] reworked the data of [41Uye] and showed that vaporization occurred by essentially complete decomposition to monatomic Cd and O_2. Because solid CdO has a small range of compositions, a transient in establishing the congruently vaporizing composition may occur, but it was usually ignored in vapor-pressure measurements. Although sensitive measurements (see later, this section) have detected CdO traces, the [51Bre] conclusion is essentially valid and was accepted in subsequent vapor-pressure measurements for CdO by [56Gil], [63Gle], [68Kod], [74Coy], [75Mil], and [81Beh]. Among these investigations those of [68Kod] and [81Beh] were regarded by the respective investigators as less accurate than those of their predecessors. The other four sets of data: [56Gil] (entrainment, 877 to 1101 °C), [63Gle] (entrainment, 969 to 1106 °C), [74Coy] (effusion-weight loss, 616 to 837 °C), and [75Mil] (effusion-weight loss, 741 to 915 °C), are only partly overlapping in temperature but are quite concordant. This is evident when they

are plotted together [81Beh] in the form of log K vs $1/T$, where

$K = P_{Cd} \times P_{O_2}^{1/2}$, the equilibrium constant, and P represents partial pressure in the gas, for the reaction:

$$CdO(s) = Cd(g) + 0.5O_2(g)$$
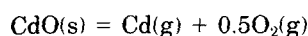
The equilibrium constant can be calculated conveniently by combining the thermodynamic data for formation of Cd(g) and of CdO(s) tabulated in the compilation of [82Pan].

The small pressure of CdO(g) over solid CdO was first measured by [78Gra] using mass-spectrometric examination of the effused products of CdO vaporization at about 900 to 1030 °C. [84Kaz] performed similar experiments between 707 and 1064 °C, but could detect CdO(g) only above 1027 °C, so measurements were for 1027 to 1064 °C only. [81Beh] tabulated the increments in thermodynamic properties of CdO(g) above 25 °C and noted that the value ΔH_f^0(CdO(g), 25 °C) $\geq$113.8 kJ/mol CdO. The compilation of [83Ped] listed a value of 126 kJ/mol CdO for this same enthalpy of formation, but the listed uncertainty is large.

There have been no investigations in which CdO specimens were chemically analyzed after equilibration at known Cd and O_2 activities. Moreover, in most of the experiments described below, in which flowing gases were used to vary CdO composition, either the activity of Cd or of O_2 in the gas was controlled, but not both, so that equilibrium between solid and gas was not actually achievable. Although [72Hay] was exceptional in using both Cd and O_2 in flowing gas to grow crystals, equilibrium was not achieved. [33Bau] showed that the electrical conductivity of CdO increased systematically with increasing partial pressure of Cd vapor. A quantitative fit to a model involving Cd^{2+} interstitials was not obtained, however, and the amount of excess Cd above the stoichiometric was not estimated. From experimental diffusion data, employing a model relating O^{2-} vacancies to O_2 activity, [62Hau] estimated that the fraction of O^{2-} vacancies in the anion sublattice at 787 °C and 0.016 MPa O_2 was 4.4×10^{-4}, corresponding to CdO with 49.989 at.% O. [67Fin] reported electron concentrations in CdO annealed at 600 to 1270 °C and quenched, but compositions were not reported. [70Kof] also reported carrier concentrations that were determined from electrical properties in CdO specimens quenched after heating at 605 to 827 °C in O_2 at pressures from 0.1 to 2.3×10^{-5} MPa, but he did not calculate compositions. [71Kof] reported the number of O^{2-} vacancies or Cd^{2+} interstitials per unit volume at RT* for these specimens. [72Hay] also gave electron concentrations from electrical conductivity and Hall effect measurements on CdO crystals annealed in air at temperatures up to about 740 °C. These concentrations were not converted to compositions. A group of CdO crystals that were chemically analyzed by [72Hay] contained 49.90 at.% O, but the conditions of preparation were not defined. It would be possible to convert some of the foregoing carrier-concentration data for particular temperatures and O_2 fugacities into compositions, but it appears improper and possibly

*Compositions at temperature might be estimated by use of density values for CdO at 605 to 827 °C calculated with the [72Str] data for thermal expansion.

misleading to make assumptions that the original investigators did not make.

A quite different experimental approach, electrochemical titration, enabled [56Eng] to measure the deviation from stoichiometric composition of a CdO specimen. Thus, it was determined that CdO sintered in air (0.021 MPa O_2) at 650 °C contained 49.986 at.% O.

The thermochemical and thermophysical properties of CdO_2 are apparently undetermined. However, [62Rop] observed by DTA that the thermal decomposition of CdO_2 into CdO and O_2, which began at 100 to 200 °C, was exothermic, in contrast to the endothermic decomposition observed with ZnO_2 and alkaline-earth peroxides. [63Wil] estimated the standard enthalpy of formation of CdO_2 to be -251 kJ/mol CdO_2 at 25 °C.

There are no thermodynamic data for oxides other than CdO and CdO_2.

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