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SCANDIUM: THERMODYNAMIC PROPERTIES, CHEMICAL EQUILIBRIA, AND STANDARD POTENTIALS

JOHN G. TRAVERS, INGEMAR DELLIEN* AND LOREN G. HEPLER
Department of Chemistry, University of Lethbridge, Lethbridge, Alberta (Canada)
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ABSTRACT

We have gathered, critically evaluated, calculated, and tabulated thermodynamic properties and related equilibrium constants and standard potentials for compounds and aqueous species of scandium. We have been explicit about sources of data so that interested readers can check the steps leading to tabulated thermodynamic quantities and thus form their own opinions about reliability and accuracy.

INTRODUCTION

In this paper we are concerned with the thermodynamic properties of scandium, its compounds, and various aqueous species derived from scandium. Thermodynamic data for all of these are useful in chemistry and applications of chemical principles to other disciplines such as metallurgy. Because many of these thermodynamic data are most useful when presented in the form of equilibrium constants or standard potentials, we have listed several of these quantities that are related to our tabulated free energies.

We have been critical in our tabulations and have recalculated many of the published results cited here. When data from several sources are in poor agreement, we have attempted to justify our choices. We have been explicit about the sources and treatment of data so that interested readers can check the steps leading to tabulated thermodynamic properties (also related equilibrium constants and standard potentials) and form their own opinions about reliability and accuracy.

In several cases we have combined experimental results from a cited source with an estimate of some thermodynamic property. *Numerical values of estimates are given in parentheses.* We have consistently used auxiliary thermodynamic data [such as ΔH_f° for Cl^-(aq), etc.] from the National Bureau of Standards[1].

In spite of considerable discussion, general agreement is still lacking on "sign conventions" for potentials. Confusion arises because "sign" can be either electrical or algebraic, as previously discussed[2]. All potentials listed here are reduction potentials with algebraic signs, and may also be taken to be electrode potentials with electrical signs relative to the standard hydrogen electrode.

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*Permanent address: Chemical Center, Physical Chemistry I, University of Lund, Lund, Sweden.

The symbols E° and K are ordinarily used for potentials and equilibrium constants that have been determined in very dilute solutions or in such ways that activity coefficients could be considered in treating the experimental results. Similarly, we use ΔG°, ΔH°, and S° to indicate quantities that refer to the usual standard states[1,3,4]. Other useful investigations have been carried out with solutions maintained at constant ionic strength by means of an "inert" supporting electrolyte. In some such cases it has been possible to make reasonable adjustments to obtain values that refer to the usual standard states. In other cases we adopt properties based on "uncorrected" data and call attention to the fact that the cited properties refer to solutions having some stated ionic strength.

Except where explicitly stated otherwise, all thermodynamic properties cited here refer to 298.15 K (25 °C).

GENERAL CHEMISTRY OF SCANDIUM

Nearly all of the chemistry of scandium is concerned with the +3 oxidation state. The Sc^{3+} ion has the configuration $\ldots 3s^2 3p^6$, is larger than Al^{3+}, and is smaller than the M^{3+} rare earth ions. As might be expected, the oxide of scandium is less acidic than Al_2O_3, but more acidic than Y_2O_3 or La_2O_3.

Among compounds that may be precipitated from aqueous solutions are the hydroxide, the fluoride (appreciably soluble in excess F^-), $ScHP_2O_7 \cdot 3H_2O$, and several double salts. Scandium hydroxide is not completely precipitated by ammonia, presumably because of complex ion formation.

Although organic complexes of Sc(III) [also Y(III), La(III), and the other rare earths] are important because of their role in the separation chemistry of these elements, we are here mostly concerned with the "inorganic" chemistry of scandium.

THERMODYNAMIC DATA

Our best general source of thermodynamic data for elementary scandium, its compounds, and its aqueous species is the National Bureau of Standards Technical Note 270-5[5], to which we frequently refer as NBS 270-5.

We follow NBS 270-5 in taking $\Delta G_f^\circ \equiv 0$ and $\Delta_f^\circ H \equiv 0$ for Sc(c) at 298 K. Heat capacity measurements from 6 to 350 K by Gerstein et al.[6] lead to $S^\circ = 8.31$ cal K^{-1} mol^{-1} for Sc(c) at 298 K, which is the value we adopt for our Table 1. This value is in reasonable agreement with $S^\circ = 8.20$ cal K^{-1} mol^{-1} reported by Weller and Kelley[7] on the basis of C_p measurements down to 50 K and with $S^\circ = 8.28$ cal K^{-1} mol^{-1} previously selected in NBS 270-5.

Calorimetric measurements[8] have led to reported values of $(H_T^\circ - H_{298}^\circ)$ and related quantities for elementary scandium up to 1600 K.

High temperature vapor pressure results from Spedding et al.[9] lead to $\Delta H_f^\circ = 82$ kcal mol^{-1} for Sc(g) at 298 K by a second law calculation and to $\Delta H_f^\circ = 90$ kcal mol^{-1} by a third law calculation. Krikorian[10] has reported $\Delta H_f^\circ =$

TABLE I

THERMODYNAMIC PROPERTIES OF SCANDIUM AT 298 K[a]

Substance	ΔH_f° (*kcal mol^{-1}*)	ΔG_f° (*kcal mol^{-1}*)	S° (*cal K^{-1} mol^{-1}*)
Sc(c)	*0*	*0*	8.31 (ref. 6)
Sc(g)	$91._1$ (refs. 10–12)	$81._1$	41.75 (ref. 13)
Sc^{+}(g)	241.5^b		
Sc^{2+}(g)	536.7^b		
Sc^{3+}(g)	1107.7^b		
Sc^{3+}(aq)	*$-146._8$*	*$-140._2$*	*−61*
Sc^{4+}(g)	2801.9^b		
Sc_2(g)	146 (ref. 15)	133	*61*
ScO(g)	-12.9^c (ref. 16)	−19.1	*53.65*
Sc_2O(g)	-5.3^c (ref. 16)		
Sc_2O_3(c)	*−456.2* (refs. 21, 22)	*−434.8*	*18.4* (ref. 18)
$Sc(OH)^{2+}$(aq)		−191 (refs. 26–32)	
$Sc(OH)_3$(ppt)		−293 (refs. 33–35)	
ScF(g)	$-32._4$ (refs. 38, 39)	$-38._5$	*53.1* (ref. 40)
ScF^{2+}(aq)		−216 (ref. 48)	
ScF_2(g)	−155 (refs. 38, 39)	−158	66 (refs. 5, 40)
ScF_2^+(aq)		−291 (ref. 48)	
ScF_3(c)	−394 (ref. 41)	−376 (ref. 41)	*22* (ref. 41)
ScF_3(g)	−306 (refs. 46, 47)	−303	70
ScF_3(aq, undissoc)		−364 (ref. 48)	
ScF_4^-(aq)		−434 (ref. 48)	
$(NH_4)ScF_4$(c)	~−517 (ref. 50)	~−471 (ref. 50)	~36 (ref. 50)
$(NH_4)_3ScF_6$(c)	~−739 (ref. 50)	~−640 (ref. 50)	~76 (ref. 50)
ScCl(g)	27.7^c	21.3^c	*56.00*
$ScCl^{2+}$(aq)		$-174._2$ (ref. 60)	
$ScCl_2$(g)			*72.5*
$ScCl_2^+$(aq)		$-207._7$ (ref. 60)	
$ScCl_3$(c)	*$-221._1$*	$-202._2$	25
$ScCl_3$(g)	−157 (refs. 53–55)	−153	76.5 (ref. 40)
$(ScCl_3)_2$(g)	−361	−343	118
$ScCl_3 \cdot 6H_2O$(c)	−668.9 (ref. 59)		
ScOCl(c)	−232 (ref. 62)	−218	(14)
$Sc(OH)_2Cl$(ppt)		−276 (ref. 36)	
$Sc_2(OH)_5Cl$(ppt)		−571 (ref. 36)	
$Sc(ClO_3)^{2+}$(aq)		$-141._0$ (ref. 61)	
$ScCl_3 \cdot 4NH_3$(c)	−338 (ref. 25)	$-249._5$ (ref. 25)	(~70)
$ScCl_3 \cdot 5NH_3$(c)	−362 (ref. 25)	$-256._7$ (ref. 25)	(~82)
$ScCl_3 \cdot 7NH_3$(c)	−406 (ref. 25)	$-266._7$ (ref. 25)	(~106)
ScBr(g)			58.6 (ref. 40)
$ScBr^{2+}$(aq)		$-167._9$ (ref. 60)	
$ScBr_2$(g)			*77.6*
$ScBr_2^+$(aq)		$-194._1$ (ref. 60)	
$ScBr_3$(c)	*$-177._6$* (ref. 24)		
$ScBr_3$(g)			84.6 (ref. 40)
$Sc(BrO_3)^{2+}$(aq)		$-140._7$ (ref. 61)	
$Sc(BrO_3)_2^+$(aq)		$-140._4$ (ref. 61)	
ScI(g)			60.5 (ref. 40)
ScI_2(g)			*81.6*

(*Table continued on p. 92*)

TABLE 1 (*continued*)

Substance	ΔH_f° (*kcal mol^{-1}*)	ΔG_f° (*kcal mol^{-1}*)	S° (*cal K^{-1} mol^{-1}*)
ScI_3(g)			90.8 (ref. 40)
ScS(g)	$43._3$ (refs. 64, 65)	$31._3$ (refs. 64, 65)	*56.3*
$Sc(SO_4)^+$ (aq)	$-357._8$ (ref. 66)	$-323._7$ (ref. 66)	−17 (ref. 66)
$Sc(SO_4)_2^-$ (aq)	$-571._2$ (ref. 66)	$-503._9$ (ref. 66)	9 (ref. 66)
ScSe(g)	$53._2$	$41._0$	(59.5) (ref. 68)
$Sc(SeO_4)^+$ (aq)		$-\mathit{248}._2$ (ref. 35)	
$Sc(SeO_4)_2^-$ (aq)		$-\mathit{354}._7$ (ref. 35)	
ScTe(g)	$66._7$ (ref. 70)	$54._4$	(61.4) (ref. 68)
$Sc(NO_3)^{2+}$ (aq)		$-\mathit{168}._4$ (ref. 71)	
ScAs(c)	$-\mathit{64}$ (ref. 73)		
ScSb(c)	−31 (ref. 74)		
ScC_2(g)	152 (ref. 75)		
ScC_4(g)	198 (ref. 75)		

[a] All values in italics are the same as listed in NBS 270-5 (ref. 5). All of our values are consistent with auxiliary data from NBS 270-3 (ref. 1). Estimated values are in parentheses. [b] These four quantities, which refer to 0 K, are 0.8 kcal mol^{-1} larger than corresponding quantities in NBS 270-5 because of the difference in ΔH_f° values there and here for Sc(g). [c] Taken from NBS 270-5, adjusted for change in ΔH_f° of Sc(g).

91.1 kcal mol^{-1}; our recalculation with more recent auxiliary data leads to $\Delta H_f^\circ =$ 91.2 kcal mol^{-1}. The similar experimental results of Habermann and Daane[11] lead to $\Delta H_f^\circ = 92.2$ kcal mol^{-1} and 91.0 kcal mol^{-1} by second and third law calculations, respectively. Finally, we also have $\Delta H_f^\circ = 91.0$ kcal mol^{-1} from more recent work by Spedding et al.[12]. We adopt $\Delta H_f^\circ = 91._1$ kcal mol^{-1} for Sc(g) at 298 K, as compared to 90.3 kcal mol^{-1} in NBS 270-5. We also adopt $S^\circ = 41.75$ cal K^{-1} mol^{-1} for Sc(g) as listed by Kelley and King[13] and in NBS 270-5. Combination of tabulated quantities now leads to $\Delta G_f^\circ = 81._1$ kcal mol^{-1} for Sc(g).

The NBS 270-5 lists ΔH° values (for 0 K) for all Sc_2^{n+}(g) [$n = 1$ to 15]. We increase their values by 0.8 kcal mol^{-1} to conform with our ΔH° for Sc(g) and list the values for $n = 1$ to 4 in our Table 1.

The properties listed in NBS 270-5 for Sc_2(g) are in close agreement with the results of Verhaegen et al.[14]. More recent publications by Drowart[15] attribute greater stability to Sc_2(g) and lead to the ΔH_f° in our Table 1.

The properties listed in NBS 270-5 for ScO(g) and Sc_2O(g) are consistent with the high temperature results of Drowart and others[16]. We adopt these properties after adjustment to conform with our ΔH_f° of Sc(g).

Work and Eick[17] have presented results of their measurements and thermodynamic calculations to contradict an earlier report of formation of ScO(c) at high temperatures. Their results[17] include some evidence for a non-stoichiometric oxynitride, ScO_xN_y(c).

For Sc_2O_3(c) we adopt $S^\circ = 18.4$ cal K^{-1} mol^{-1} from the heat capacity measurements of Weller and King[18], as also listed in NBS 270-5. Even careful workers with considerable experience have had difficulties with determination of ΔH_f° of Sc_2O_3(c). For example, Mah[19] has reported $\Delta H_f^\circ = -447.3$ kcal mol^{-1} on the basis of combustion measurements, but subsequently[20] found that the alundum disk used to support the scandium metal for combustion affected the results. More recently Huber et al.[21] have reported $\Delta H_f^\circ = -456.16 \pm 0.50$ kcal mol^{-1} on the basis of combustion calorimetry and $\Delta H_f^\circ = -458.3 \pm 0.7$ kcal mol^{-1} from solution calorimetry. Holley et al.[22] suggest that this latter value is probably too negative because the Sc_2O_3(c) used in the solution calorimetry experiments was not fired at a sufficiently high temperature. We therefore adopt $\Delta H_f^\circ = -456.2$ kcal mol^{-1} for Sc_2O_3(c) and combine with the above S° to obtain its $\Delta G_f^\circ = -434.8$ kcal mol^{-1}. We also note that high temperature calorimetric measurements by Pankratz and Kelley[23] lead to values of $(H_T^\circ - H_{298}^\circ)$ and related thermodynamic functions for Sc_2O_3(c).

We use the ΔH_f° for $ScCl_3$(c) that is discussed below with enthalpies of solution[24,25] (not near infinite dilution) to calculate ΔH_f° values for Sc^{3+}(aq) that are both larger and smaller than the value listed in NBS 270-5. Noting that the uncertainty is several kcal mol^{-1}, we adopt $\Delta H_f^\circ = -146._8$ kcal mol^{-1} from the NBS 270-5. We are not aware of any experimental results that lead to the entropy of Sc^{3+}(aq). Because the $S^\circ = -61$ cal K^{-1} mol^{-1} (possibly an estimate) listed in NBS 270-5 seems "reasonable", we adopt it and combine with the above ΔH_f° to obtain $\Delta G_f^\circ = -140._2$ kcal mol^{-1} for Sc^{3+}(aq). This free energy corresponds to the standard potential

$$Sc^{3+}(aq) + 3e^- = Sc(c) \qquad E^\circ = -2.0_2 \text{ V}$$

In connection with the ΔH_f° (and thence the ΔG_f°) for Sc^{3+}(aq), note the further discussion later in connection with $ScCl_3 \cdot 6H_2O$(c).

Among the first thorough studies of the hydrolysis reactions of a metal ion were those of Kilpatrick and Pokras[26] on Sc^{3+}(aq). Their results provided evidence for both $Sc(OH)^{2+}$(aq) and the hydrolytic dimer $Sc_2(OH)_2^{4+}$(aq). Equilibrium constants were evaluated at three temperatures for formation reactions involving these species and approximate values of corresponding enthalpies and entropies were calculated. Aveston's later results[27] (interpreted in terms of monomers, dimers, and trimers) have provided general support for the picture first suggested by Kilpatrick and Pokras[26]. Still further support has been provided by the equilibrium investigation of Akalin and Özer[28] and the kinetic results of Cole et al.[29]. Results of three investigations[30–32] involving very dilute scandium solutions have been interpreted in terms of monomeric species. One of these investigations[32] was also concerned with hydrolysis of Sc^{3+}(aq) in H_2O–EtOH mixed solvent systems.

The free energies in NBS 270-5 lead to $K = 1.1 \times 10^{-4}$ for the first hydrolysis represented by

$$Sc^{3+}(aq) + H_2O(liq) = Sc(OH)^{2+}(aq) + H^+(aq)$$

Our own extrapolation to infinite dilution of the results cited above[26–32] or the equivalent estimation of activity coefficients lead us to suggest that a somewhat smaller $K \cong 0.4 \times 10^{-4}$ may be better. Because equilibrium constants chosen for subsequent hydrolysis to such species as $Sc_2(OH)_2^{4+}(aq)$ and $Sc(OH)_2^+(aq)$ depend on the value adopted for the equilibrium represented by the equation above, we refer interested readers to the original papers for such constants that are internally consistent with particular experimental results and assignment of reactions. Cumulative uncertainties in all of this difficult work lead us to omit enthalpies and entropies for $Sc(OH)^{2+}(aq)$ from our Table 1.

Because of hydrolysis and polymerization of $Sc^{3+}(aq)$ as pH increases, it is difficult to interpret solubility data for scandium hydroxide. A wide range of solubility products has been reported. Free energies in NBS 270-5 lead to $K_{sp} = 2 \times 10^{-31}$, which is close to the value reported by Oka[33]. More recent work carried out and reviewed by Aksel'rud[34] suggests $K_{sp} = 2 \times 10^{-30}$. Sillén[35] have quoted $K_{sp} = 9 \times 10^{-30}$ from the work of Kovalenko and Bagdasarov. On the basis of all of these investigations we adopt the following:

$$Sc(OH)_3(ppt) = Sc^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = 4 \times 10^{-30}$$

This solubility product leads us to $\Delta G_f^\circ = -293$ kcal mol^{-1} for $Sc(OH)_3(ppt)$ and thence to the following potential:

$$Sc(OH)_3(ppt) + 3e^- = Sc(c) + 3OH^-(aq) \qquad E^\circ = -2.6_0\ V$$

Our free energies (Table 1) correspond to

$$\tfrac{1}{2}Sc_2O_3(c) + 1.5H_2O(liq) = Sc^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = 4 \times 10^{-37}$$

These K_{sp} and ΔG_f° values for $Sc(OH)_3(ppt)$ and $Sc_2O_3(c)$ are consistent with the observation that $Sc(OH)_3(ppt)$ is unstable with respect to the oxide and water and that the solubility of precipitated scandium hydroxide decreases on aging. The calculated potential for the Sc_2O_3/Sc couple is

$$Sc_2O_3(c) + 3H_2O(liq) + 3e^- = 2Sc(c) + 6OH^-(aq) \qquad E^\circ = -2.74\ V$$

Sillén[36] have cited equilibrium investigations by Aksel'rud that lead to the following:

$$Sc(OH)_2Cl(ppt) = Sc^{3+}(aq) + 2OH^-(aq) + Cl^-(aq) \qquad K_{sp} = 2.2 \times 10^{-22}$$

$$Sc_2(OH)_5Cl(ppt) = 2Sc^{3+}(aq) + 5OH^-(aq) + Cl^-(aq) \qquad K_{sp} = 4.6 \times 10^{-53}$$

We use these values in calculating $\Delta G_f^\circ = -276$ kcal mol^{-1} for $Sc(OH)_2Cl(ppt)$ and $\Delta G_f^\circ = -571$ kcal mol^{-1} for $Sc_2(OH)_5Cl(ppt)$. The former value is in good agreement with the corresponding ΔG_f° in NBS 270-5, but it appears that there is an error in the ΔG_f° listed there for $Sc_2(OH)_5Cl(ppt)$. The equilibrium constants above and the free energies we have calculated are consistent with the observation that the basic chloride precipitates are converted to the hydroxide in alkaline solution, as indicated by the following:

$$\mathrm{Sc(OH)_2Cl(ppt)+OH^-(aq) = Sc(OH)_3(ppt)+Cl^-(aq)} \qquad K=8\times10^7$$

$$\mathrm{Sc_2(OH)_5Cl(ppt)+OH^-(aq) = 2Sc(OH)_3(ppt)+Cl^-(aq)} \qquad K=3\times10^6$$

In the absence of calorimetric data, we must rely upon the results of equilibrium investigations for the thermodynamic properties of scandium hydride. Unfortunately, these investigations are sufficiently difficult that results of different workers are not in good agreement. Further, it is difficult to interpret the published results. One measure of the collective difficulties is provided by the substantially different thermodynamic properties that have been calculated. For example, the NBS 270-5 lists $\Delta H_f^\circ = -32.2$ kcal mol^{-1} for $ScH_{1.97}(c)$, while Beavis[37] (who cites references to earlier papers) has calculated $\Delta H_f^\circ = -47.8$ kcal mol^{-1} for $ScH_2(c)$. Because we are unable to justify any particular choice as "best", we omit scandium hydride from our Table 1.

Zmbov and Margrave[38] have made dissociation energy measurements on ScF(g), $ScF_2(g)$, and $ScF_3(g)$, all relative to CaF(g). We have combined their published results with properties of CaF(g) from NBS Tech. Note 270-6[39] to obtain $\Delta H_f^\circ = -32._4$ kcal mol^{-1} for ScF(q) and $\Delta H_f^\circ = -155$ kcal mol^{-1} for $ScF_2(g)$. The NBS 270-5 and Krasnov and Danilova[40] have listed S° values at 298 K for these species. Our choices for these entropies and also the related free energies are listed in Table 1 for both ScF(g) and $ScF_2(g)$.

We have several routes to the thermodynamic properties of $ScF_3(c)$ and $ScF_3(g)$, as described below.

Rezukhina et al.[41] have made high temperature emf measurements that are consistent with $\Delta G_f^\circ = -376$ kcal mol^{-1}, $\Delta H^\circ = -394$ kcal mol^{-1}, and $S^\circ = 22$ cal K^{-1} mol^{-1} for $ScF_3(c)$ at 298 K. Other high temperature emf results from Skelton and Patterson[42] permit us to calculate $\Delta G_f^\circ = -362$ kcal mol^{-1}, $\Delta H_f^\circ = -375$ kcal mol^{-1}, and $S^\circ = 36$ cal K^{-1} mol^{-1}, all for $ScF_3(c)$ at 298 K. Both of the entropy values above are considerably larger than $S^\circ = (16.88)$ cal K^{-1} mol^{-1} estimated by Spedding et al.[43] by a method that has proven reliable for some other compounds. A third law entropy for $ScF_3(c)$ based on C_p measurements would be useful, as would a modern calorimetrically determined ΔH_f°.

We also call attention to some high temperature investigations of vapor pressures of $ScF_3(c)$. The results of Fischer and Lange[44] appear to contain substantial errors. Other investigators[45–47] have reported results that lead to reported enthalpies of vaporization of $ScF_3(c)$ at 298 K as follows: 101 ± 5, 87 ± 1, and 88.5 ± 2.3 kcal mol^{-1}. The ΔH_f° values in NBS 270-5 correspond to 89 kcal mol^{-1} for this enthalpy of vaporization.

Dissociation energy measurements [relative to CaF(g)] by Zmbov and Margrave[38] lead (as above) to $\Delta H_f^\circ = -295$ kcal mol^{-1} for $ScF_3(g)$.

We also note that Krasnov and Danilova[40] report $S^\circ = 68.487$ cal K^{-1} mol^{-1} for $ScF_3(g)$, as compared to $S^\circ = 71.8$ cal K^{-1} mol^{-1} that is listed in NBS 270-5.

There is no single set of thermodynamic properties of ScF_3(c) and ScF_3(g) that is consistent with all of the results cited above. The best that we can do is make "reasonable" choices, based on our partly arbitrary preferences for the most recent high temperature emf[41] and vapor pressure[46,47] results. Our choices are listed in Table 1.

Spedding et al.[43] have made high temperature calorimetric measurements leading to $(H_T^\circ - H_{298}^\circ)$ and related thermodynamic quantities [based on their $S^\circ = (16.88)$ cal K^{-1} mol^{-1}] for ScF_3(c).

Potentiometric measurements on Fe^{3+}/Fe^{2+} concentration cells have led to equilibrium constants (0.5 M $NaClO_4$) and thence with estimated activity coefficients to the following[48]:

$Sc^{3+}(aq) + F^-(aq) = ScF^{2+}(aq)$ $K = 1.2 \times 10^7$

$ScF^{2+}(aq) + F^-(aq) = ScF_2^+(aq)$ $K = 6.4 \times 10^5$

$ScF_2^+(aq) + F^-(aq) = ScF_3(aq)$ $K = 3.0 \times 10^4$

$ScF_3(aq) + F^-(aq) = ScF_4^-(aq)$ $K = 7 \times 10^2$

Estimates of enthalpies and entropies for the above reactions have been based on equilibrium constants[48] from 15–35°C. Subsequent measurements[49] with a fluoride specific ion electrode have led to equilibrium constants in agreement with those above. There is some evidence for ScF_5^{2-} and ScF_6^{3-}, but we are unable to cite any thermodynamic properties.

High temperature results from Mikhailov et al.[50] lead to the approximate values we list in Table 1 for $(NH_4)ScF_4$(c) and $(NH_4)_3ScF_6$(c).

Shcheredin and Sidorov[51] have made measurements leading to $\Delta H \cong$ 31.0 kcal mol^{-1} for melting $(NaF)_3 \cdot ScF_3$(c). We are unable to list other properties of this compound.

For $ScCl_3$(c) we have $\Delta H_f^\circ = -221.1$ kcal mol^{-1} from NBS Tech. Note 270-5 and $\Delta H_f^\circ = -225.4$ kcal mol^{-1} from Stuve[52]. The former value is consistent with enthalpies of solution of Sc(c) and $ScCl_3$(c) reported by Bommer and Hohmann[24], while the latter value is based on enthalpies of solution of Sc_2O_3(c) and $ScCl_3$(c). In the absence of further definitive measurements, we follow NBS 270-5 and adopt $\Delta H_f^\circ = -221._1$ kcal mol^{-1} for $ScCl_3$(c) for our Table 1.

Results of investigations of the vaporization of $ScCl_3$(c) and the dimerization of $ScCl_3$(g) are only in fair agreement. Vapor pressure measurements by Dudchik et al.[53] led (without consideration of dimerization) to $\Delta H^\circ = 67$ kcal mol^{-1} and $\Delta S^\circ = 56$ cal K^{-1} mol^{-1} for vaporization of $ScCl_3$(c) at 298 K. More recent measurements by Rat'kovskii et al.[54] led to $\Delta H^\circ = 65.7$ kcal mol^{-1} and $\Delta S^\circ = 57.7$ cal K^{-1} mol^{-1} for the same vaporization process, with allowance apparently made for dimerization. We have used the vapor pressure equation reported by Patrikeev et al.[55] to calculate $\Delta H^\circ = 63.4$ kcal mol^{-1} and $\Delta S^\circ = 46$ cal K^{-1} mol^{-1} for vaporization, with allowance made for dimers. We also have a calculated

$S^\circ = 76.549$ cal K^{-1} mol^{-1} for $ScCl_3(g)$ from Krasnov and Danilova[40] and various "reasonable" methods for estimating the entropy of $ScCl_3(c)$. We choose $S^\circ = 76.5$ cal K^{-1} mol^{-1} for $ScCl_3(g)$. $\Delta H^\circ = 64$ kcal mol^{-1} and $\Delta S^\circ = 51._5$ cal K^{-1} mol^{-1} for vaporization to monomer, $S^\circ = 25$ cal K^{-1} mol^{-1} for $ScCl_3(c)$, and the corresponding properties for $ScCl_3$(c and g) listed in our Table 1.

Schäfer and Binnewies[56] have carried out a high temperature mass spectrometric investigation of dimerization of $ScCl_3(g)$ and have reported $\Delta H^\circ = -48.8$ kcal mol^{-1} and $\Delta S^\circ = -36.0$ cal K^{-1} mol^{-1} for

$$2ScCl_3(g) = (ScCl_3)_2(g)$$

at 298 K. They also quote $\Delta H^\circ = -47.1$ kcal mol^{-1} and $\Delta S^\circ = -37.0$ cal K^{-1} mol^{-1} for this reaction from the work of Patrikeev et al.[55], but our calculations with the published[55] vapor pressure equations lead to $\Delta H^\circ = -45.6$ kcal mol^{-1} and $\Delta S^\circ = -31.8$ cal K^{-1} mol^{-1}. Although Rat'kovskii et al. evidently obtained data for $(ScCl_3)_2(g)$, the short summary[54] of their results does not permit us to calculate quantities to compare with those we cite here. Our selected properties of $(ScCl_3)_2(g)$ are listed in Table 1.

Dworkin and Bredig[57] have measured $(H_T - H_{298})$ for $ScCl_3$ up to 1273 K (melting point is 1240 K).

McCollum et al.[58] have investigated the Sc–$ScCl_3$ system and reviewed earlier work. They[58] report convincing evidence for $Sc_2Cl_3(c)$ and contradict earlier reports of other low oxidation state scandium chlorides. For $ScCl(g)$ and $ScCl_2(g)$ we adopt the properties listed in NBS 270-5, and note that similar entropies have been calculated by Krasnov and Danilova[40].

Maier et al.[59] have reported $\Delta H = -7.06$ kcal for dissolving one mole of $ScCl_3 \cdot 6H_2O(c)$ in 2580 moles of H_2O(liq). We estimate the enthalpy of dilution to obtain $\Delta H^\circ = -7.6$ kcal mol^{-1} and combine with the ΔH_f° for Sc^{3+}(aq) cited earlier to obtain $\Delta H_f^\circ = -668.9$ kcal mol^{-1} for $ScCl_3 \cdot 6H_2O(c)$. We compare these values with properties in NBS 270-5 in two ways. First, we use the NBS 270-5 enthalpy of formation of $ScCl_3$ in 5500 H_2O with our estimated enthalpy of dilution and the NBS 270-5 ΔH_f° of $ScCl_3 \cdot 6H_2O(c)$ to obtain $\Delta H^\circ = -7.6$ kcal mol^{-1} for dissolving $ScCl_3 \cdot 6H_2O(c)$, in agreement with the ΔH° we have obtained above. Second, we combine the ΔH_f° for Sc^{3+}(aq) from their ΔH_f° of $ScCl_3 \cdot 6H_2O(c)$ to obtain $\Delta H^\circ = -4.9$ kcal mol^{-1} for dissolving $ScCl_3 \cdot 6H_2O(c)$. In order to maintain consistency between the calorimetric enthalpy of solution[59] and the ΔH_f° of Sc^{3+}(aq) listed in NBS 270-5 and adopted for our Table 1, it is necessary to reject the NBS 270-5 ΔH_f° value for $ScCl_3 \cdot 6H_2O(c)$ and accept instead the value we have listed earlier in this paragraph. Because we might have maintained consistency by rejecting the ΔH_f° for Sc^{3+}(aq) that was listed in NBS 270-5 and is also adopted here for our Table 1, we must recognize that this latter quantity may be in error, which might also involve an error in the ΔH_f° of $ScCl_3(c)$.

Orlovskii and Tananaev[25] have reported that the equilibrium pressure of $NH_3(g)$ over a mixture of $ScCl_3 \cdot 5NH_3(c)$ and $ScCl_3 \cdot 4NH_3(c)$ is 2.60–2.90 mm Hg and that the pressure over a mixture of $ScCl_3 \cdot 7NH_3(c)$ and $ScCl_3 \cdot 5NH_3(c)$ is 126 mm Hg, both at 25°C. Their calorimetric results also lead us to the following:

$$ScCl_3(c) + 4NH_3(g) = ScCl_3 \cdot 4NH_3(c) \qquad \Delta H^\circ = -73 \text{ kcal mol}^{-1}$$

$$ScCl_3(c) + 5NH_3(g) = ScCl_3 \cdot 5NH_3(c) \qquad \Delta H^\circ = -86 \text{ kcal mol}^{-1}$$

$$ScCl_3 \cdot 5NH_3(c) = ScCl_3 \cdot 4NH_3(c) + NH_3(g) \qquad \Delta H^\circ = 13 \text{ kcal mol}^{-1}$$

Our combination of this third ΔH° with ΔG° from the equilibrium vapor pressure cited above leads to $\Delta S^\circ \cong 32$ cal K^{-1} mol^{-1} for this reaction, which seems to be a "reasonable" value.

We now use the ΔH_f° values above to calculate $\Delta H_f^\circ = -338$ kcal mol^{-1} for $ScCl_3 \cdot 4NH_3(c)$ and $\Delta H_f^\circ = -362$ kcal mol^{-1} for $ScCl_3 \cdot 5NH_3(c)$. Combination of these ΔH_f° values with estimated entropies leads to the corresponding ΔG_f° values that are listed in Table 1. We also use the second equilibrium vapor pressure given above with the ΔG_f° of $ScCl_3 \cdot 5NH_3(c)$ to calculate the ΔG_f° of $ScCl_3 \cdot 7NH_3(c)$. Combination of this latter ΔG_f° with an estimated entropy leads to the tabulated ΔH_f° of $ScCl_3 \cdot 7NH_3(c)$.

The ΔG_f° for $ScCl^{2+}(aq)$ listed in NBS 270-5 corresponds to $K_1 = 6.7$ for formation of this ion from $Sc^{3+}(aq)$ and $Cl^-(aq)$. Paul's[60] measurements lead to $K_1 = 11.7$ for this reaction in 0.5 M $NaClO_4$ solution and she has calculated $K_1 = 90$ for infinitely dilute solution. The NBS 270-5 ΔG_f° for $ScCl_2^+(aq)$ corresponds to $K_2 = 26$ for formation of this ion from $ScCl^{2+}(aq)$ and $Cl^-(aq)$ as compared to $K_2 = 10.9$ for 0.5 M $NaClO_4$ and $K_2 = 37$ for infinitely dilute solutions from Paul[60]. The K_1 and K_2 values from several other investigations cited by Sillén[35] refer to different conditions, but all are consistent with $K_2 < K_1$. We believe that Paul's[60] results are the best ones presently available and adopt the following:

$$Sc^{3+}(aq) + Cl^-(aq) = ScCl^{2+}(aq) \qquad K_1 = 90$$

$$ScCl^{2+}(aq) + Cl^-(aq) = ScCl_2^+(aq) \qquad K_2 = 37$$

We use these K values in calculating our ΔG_f° values for $ScCl^{2+}(aq)$ and $ScCl_2^+(aq)$. Paul's[60] K_1 and K_2 values at 15, 25, and 35°C permit estimates of ΔH° and ΔS° values for the corresponding reactions. Because of cumulative uncertainties, we omit these latter values from our Table 1.

Morris et al.[61] investigated formation of scandium chlorate complexes at several temperatures. For 25°C they reported the following (1 M $HClO_4$):

$$Sc^{3+}(aq) + ClO_3^-(aq) = Sc(ClO_3)^{2+}(aq) \qquad K = 0.95$$

Without trying to adjust this K value to our infinitely dilute standard state, we use it in obtaining $\Delta G_f^\circ = -141._0$ kcal mol^{-1} for $Sc(ClO_3)^{2+}(aq)$. Estimates of the enthalpy and entropy can be obtained from the variation of K with temperature. Morris et al.[61] also reported less precise K values for formation of $Sc(ClO_3)_2^+(aq)$.

Patrikeev et al.[62] have reported $\Delta H_{298}^\circ = 86.0$ kcal mol^{-1} and $\Delta S_{298}^\circ =$

62.7 cal K^{-1} mol^{-1} for the reaction

$$3\,ScOCl(c) = Sc_2O_3(c) + ScCl_3(g)$$

We combine these values with the properties listed in Table 1 for Sc_2O_3(c) and $ScCl_3$(g) to obtain $\Delta H_f^\circ = -233$ kcal mol^{-1} and $S^\circ = 11$ cal K^{-1} mol^{-1} for ScOCl(c). In order to make this entropy agree with our estimated $S^\circ = (14$ or more) cal K^{-1} mol^{-1}, it is necessary to decrease the ΔS° above by 9 (or more) cal K^{-1} mol^{-1}, which corresponds to a change of some 3 kcal mol^{-1} in ΔH° and/or ΔG°. We arbitrarily make such changes and list the resulting (quite uncertain) properties of ScOCl(c) in Table 1.

The NBS 270-5 free energies of $ScBr^{2+}$(aq) and $ScBr^{+}$(aq) lead to equilibrium constants ($K_1 = 7$ and $K_2 = 2$) in poor agreement with the results of Paul[60], from whom we adopt the following:

$$Sc^{3+}(aq) + Br^-(aq) = ScBr^{2+}(aq) \qquad K_1 = 120$$

$$ScBr^{2+}(aq) + Br^-(aq) = ScBr_2^+(aq) \qquad K_2 = 10$$

Our tabulated ΔG_f° values for $ScBr^{2+}$(aq) and $ScBr_2^+$(aq) are based on these K values. Paul's[60] K values at other temperatures lead to estimates of corresponding enthalpies and entropies that we do not list in Table 1.

McCollum et al.[58] have investigated phase relations in the Sc–$ScBr_3$ system and characterized Sc_2Br_3(c).

We adopt S° for $ScBr_2$(g) from NBS 270-5, while noting that Krasnov and Danilova[40] have calculated a slightly smaller value. Our S° values for ScBr(g) and $ScBr_3$(g) are from Krasnov and Danilova[40].

The ΔH_f° for $ScBr_3$(c) in NBS 270-5 and our Table 1 is consistent with the calorimetric results of Bommer and Hohmann[24].

Orlovskii and Tananaev[25] have reported that the equilibrium vapor pressure of NH_3(g) over a mixture of $ScBr_3 \cdot 7NH_3$(c) and $ScBr_3 \cdot 5NH_3$(c) is 94 mm Hg at 25 °C and that the equilibrium pressure over a mixture of $ScBr_3 \cdot 5NH_3$(c) and $ScBr_3 \cdot 4NH_3$(c) is less than 2 mm Hg.

Morris et al.[61] have investigated formation of scandium bromate complexes at several temperatures. For 25 °C they report the following (1 M $HClO_4$):

$$Sc^{3+}(aq) + BrO_3^-(aq) = Sc(BrO_3)^{2+}(aq) \qquad K = 4.5$$

$$Sc^{3+}(aq) + 2\,BrO_3^-(aq) = Sc(BrO_3)_2^+(aq) \qquad K = 5.6$$

Without trying to adjust these K values to our infinitely dilute standard state, we use them in obtaining $\Delta G_f^\circ = -140._7$ kcal mol^{-1} for $Sc(BrO_3)^{2+}$(aq) and $\Delta G_f^\circ = -140._4$ kcal mol^{-1} for $Sc(BrO_3)_2^+$(aq). Estimates of the enthalpy and entropy can be obtained from the variation of these equilibrium constants with temperature.

We adopt S° for ScI_2(g) from NBS 270-5, although Krasnov and Danilova[40] have calculated a smaller value. Our S° values for ScI(g) and ScI_3(g) are from

Krasnov and Danilova[40]. McCollum and Corbett[63] have reported $ScI_{2.15}$(c), which appears to have metallic properties.

Our tabulated ΔH_f° and ΔG_f° for ScS(g) are consistent with the results of Coppens et al.[64] and Steiger[65].

The NBS 270-5 ΔG_f° of $Sc(SO_4)^+$(aq) corresponds to $K_1 = 3.9 \times 10^2$ for formation of this ion from its constituent ions, in agreement with the value from Kolosov et al. cited by Sillén[35] as referring to 0.5 M $NaClO_4$ solution. Application of the same kind of activity adjustments previously used[48,60] for halide complexes leads to the conclusion that the K_1 referring to infinitely dilute solution should be substantially greater than the values referring to 0.5 M solution. Similarly, the ΔG_f° for $Sc(SO_4)_2^-$(aq) listed in NBS 270-5 leads to $K_2 = 22$, in agreement with the results of Kolosov et al.[35] for 0.5 M solution, and again we conclude that the K_2 referring to infinitely dilute solution should be greater than this value. Since the K values reported by Izatt et al.[66] (intended to refer to our infinitely dilute standard state) are qualitatively in accord with the activity adjustments suggested above, we adopt the following from their work:

$$Sc^{3+}(aq) + SO_4^{2-}(aq) = Sc(SO_4)^+(aq) \qquad K = 1.1 \times 10^4$$

$$Sc(SO_4)^+(aq) + SO_4^{2-}(aq) = Sc(SO_4)_2^-(aq) \qquad K = 46$$

These K values lead to our ΔG_f° values for $Sc(SO_4)^+$(aq) and $Sc(SO_4)_2^-$(aq) that are listed in Table 1 along with ΔH_f° and S° values that are also derived from the results of Izatt et al.[66].

For ScSe(g) we take the dissociation energy (at 0 K) from Ni and Wahlbeck[67], who have reviewed earlier determinations. Combination of this D_0° with the ΔH_f° for Se(g) from NBS 270-3 and auxiliary data for scandium and selenium from NBS 270-5 and NBS 270-3 and with $(H_{298}^\circ - H_0^\circ)$ for ScSe(g) from Mills[68] leads us to $\Delta H_f^\circ = 52._2$ kcal mol^{-1} for ScSe(g). We combine this ΔH_f° with the S° from Mills[68] to obtain our ΔG_f°.

Leary and Wahlbeck[69] have investigated the high temperature vaporization of Sc_2Se_3(c).

The NBS 270-5 ΔG_f° values for $Sc(SeO_4)^+$(aq) and $Sc(SeO_4)_2^-$(aq) correspond to the following:

$$Sc^{3+}(aq) + SeO_4^{2-}(aq) = Sc(SeO_4)^+(aq) \qquad K = 68$$

$$Sc^{3+}(aq) + 2SeO^{2-}(aq) = Sc(SeO_4)_2^-(aq) \qquad K = 368$$

These equilibrium constants are in reasonable agreement with values from Kolosov et al. quoted by Sillén[35] as referring to 0.5 M $NaClO_4$ solution. Because the ΔH_f° and S° values in NBS 270-5 are not consistent with the quoted[35] enthalpies and entropies of reaction, we omit values of these properties from our Table 1.

Maier et al.[59] have reported the enthalpy of precipitation of $Sc_2(SeO_3)_3$(amorph). We combine their result with our ΔH_f° for Sc^{3+}(aq) [or the corresponding ΔH_f° for $ScCl_3$(aq)] and the $\Delta H_f^\circ = -230.05$ kcal mol^{-1} cited by Maier et al.[60] for

Na_2SeO_3(c) to obtain $\Delta H_f^\circ = -655$ kcal mol^{-1} for $Sc_2(SeO_3)_3$(amorph). If we assume that the precipitated material was $Sc_2(SeO_3)_3 \cdot 10H_2O$ (c or amorph), we calculate its $\Delta H_f^\circ = -1338$ kcal mol^{-1}. The NBS 270-5 has listed -1326.5 kcal mol^{-1} for this latter ΔH_f°. Because we are unaware of any other relevant experimental investigations and have no way of ascertaining the "best" ΔH_f° value for Na_2SeO_3(c), we omit scandium selenite from our Table 1.

The dissociation energy of ScTe(g) from Bergman et al.[70] leads us [with ΔH_f° for Te(g) from NBS 270-3] to $\Delta H^\circ = 66._7$ kcal mol^{-1} for ScTe(g), which we combine with the entropy from Mills[68] to obtain the ΔG_f°.

The ΔG_f° for $Sc(NO_3)^{2+}$(aq) in NBS 270-5 corresponds to

$$Sc^{3+}(aq) + NO_3^-(aq) = Sc(NO_3)^{2+}(aq) \qquad K = 15$$

This value appears to be based on a reasonable activity adjustment of the equilibrium quotient reported by Morris et al.[71] for 1.0 M perchlorate solution. The K value above shows that it can be unwise to use NO_3^-(aq) as a "non-complexing" anion in investigations of Sc^{3+}(aq). The results at several temperatures reported by Morris et al.[71] permit calculation of approximate enthalpies and entropies for the reaction above.

Yaglov et al.[72] have reported $K_{sp} = 1.1 \times 10^{-27}$ for scandium orthophosphate represented by $ScPO_4$(c). This quantity has led them to ΔG_f° of $ScPO_4$(c), which has been combined with their estimated S° to yield a ΔH_f°. In the same paper[72] it is reported that scandium phosphate crystallizes from aqueous solution as the dihydrate, $Sc(PO_4)_3 \cdot 2H_2O$(c) and that $\Delta H^\circ = 34.4$ kcal mol^{-1} (from vapor pressure measurements) for dehydration of this substance. If the solid phase in equilibrium with saturated solution is indeed the dihydrate, the calculations described above for $ScPO_4$(c) are incorrect. Because further information is needed to justify thermodynamic calculations that can be taken seriously, we omit scandium phosphate from our Table 1.

The NBS 270-5 ΔH_f° for ScAs(c) is consistent with the high temperature results of Hanks and Faktor[73]. We take $\Delta H_f^\circ = -31$ kcal mol^{-1} for ScSb(c) from the work of Pratt and Chua[74].

The NBS 270-5 lists $\Delta H_f^\circ = 143.6$ kcal mol^{-1} for ScC_2(g), but we choose $\Delta H_f^\circ = 152$ kcal mol^{-1} from the work of Kohl and Stearns[75]. Their results also lead us to $\Delta H_f^\circ = 198$ kcal mol^{-1} for ScC_4(g).

Although we are here primarily concerned with inorganic compounds and ions of scandium, we provide brief mention of some organic systems as follows.

Moeller et al.[76] and Melson and Stotz[77] have written general reviews of coordination chemistry, with considerable emphasis on organic complexes. Martell[35,36] have compiled many stability constants. Most investigations of organic complexes of scandium have been limited to determination of stability contants at a single temperature. We therefore call particular attention to the work of Grenthe and Hansson[78], who made potentiometric measurements leading to K values and calorimetric measurements leading to ΔH° values for formation of malonate, diglycolate, and dipicolinate complexes of scandium.

Wood and Jones[79] have measured heats of combustion of the acetylacetonate and dibenzoylmethane complex of scandium (and other metals) and provide references to some related investigations.

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