

Mercury: Thermodynamic Properties, Chemical Equilibria, and Standard Potentials

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I. Introduction

In this review we are primarily concerned with the thermodynamic properties of mercury, its compounds, and various aqueous species derived from mercury. Thermodynamic data for all of these have long been known to be useful in electrochemistry, analytical chemistry, and many applications of chemical principles to other disciplines. Because many of these thermodynamic data are most useful when presented in the form of equilibrium constants or standard potentials, we have listed a large number of these quantities.

We have been critical in our tabulations of data and have recalculated many of the published results cited here. When data from several sources are not in good agreement, we have attempted to justify our choices. We have been explicit about the sources of data and also our treatment of data so that interested readers can check the steps leading to tabulated values of 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 data from a cited source with our estimate of some thermodynamic property. *Numerical values of our estimates are given in parentheses.*

We have used auxiliary thermodynamic data [such as ΔH_f° of $\text{Cl}^-(\text{aq})$] from the National Bureau of Standards Technical Note 270-3,² which is the most comprehensive source of such data available to us.

In spite of considerable discussion in recent years, general agreement is still lacking on "sign conventions" for potentials. Much of the confusion arises because "sign" can be either electrical or algebraic, as previously discussed.³ All potentials listed in this review are reduction potentials with algebraic signs, and may also be taken to be electrode potentials with electrical signs relative to that of the standard hydrogen electrode.

The symbols E° and K are 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 data. Similarly, we use ΔG° , ΔH° , and ΔS° to indicate data that refer to the usual standard states.^{2,4,5} Other useful investigations have been carried out in solutions maintained at some constant ionic strength by means of some "inert" supporting electrolyte. In some cases it has been possible to make reasonable estimates of corrections 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 in this review refer to 298.15 K (25°C).

II. General Chemistry of Mercury

Mercury and its compounds are widely used in both "pure" and "applied" chemistry. Further, many of the properties of mercury and its compounds are sufficiently unusual as to have attracted the attentions of numerous investigators. As a result, many aspects of the chemistry of mercury have been extensively investigated so that we have a considerable body of quantitative information to report later in this review. In recent years increased concern about the dangers of mercury in the environment has led to new investigations, some of which have yielded results that are pertinent to this review.

Various aspects of the chemistry of mercury have been reviewed in general or in ways indicated by publication titles.⁶⁻¹⁷ We also call attention to some reviews of particular aspects of the chemistry of mercury as follows: hazards of mercury,¹⁸ structural chemistry,¹⁹ and surface properties.²⁰ Recent publications²¹⁻²⁴ from the U.S. Bureau of Mines illustrate applications of research on mercury to contemporary problems. We also call attention to the new edition of the book by Cotton and Wilkinson²⁵ in which there is an excellent summary of the chemistry of mercury, with emphasis on structural and bonding problems.

We now present a brief descriptive account of some of the chemistry of mercury. Then, in the next section, we begin our detailed discussion of thermodynamic and related properties.

A large number of compounds of mercury in the +1 (mercurous) and +2 (mercuric) oxidation states are known. The absence of compounds containing mercury in oxidation states greater than +2 can be attributed to the very high third ionization potential.

The principal ore of mercury is cinnabar (red HgS), which is usually heated with oxygen or air to yield the element. The reversible decomposition-formation of HgO at moderately high temperatures was important in the early work of Lavoisier and Priestly, and also has significance with respect to the thermodynamic properties of $\text{HgO}(\text{c})$ and thence many aque-

TABLE Ia.^a Thermodynamic Properties of Mercury at 298 K

Substance	ΔH_f° , kcal mol ⁻¹	ΔG_f° , kcal mol ⁻¹	S° , cal K ⁻¹ mol ⁻¹	Substance	ΔH_f° , kcal mol ⁻¹	ΔG_f° , kcal mol ⁻¹	S° , cal K ⁻¹ mol ⁻¹
Hg(liq)	0	0	18.17 ^{30,31}	HgS(c, red)	-12.9	-11.1	19.7 ¹³⁶
Hg(g)	14.655	7.613	41.79	HgS(c, black)	-12.0	-10.6	21.2
Hg(aq)	3.33 ⁴³	8.9 ⁴³	-0.5	HgSO ₄ (c)	-169.1	-142	(34)
Hg ⁺ (g)	256.82			HgSO ₄ (aq, undiss)		-140.5 ^b	
Hg ²⁺ (g)	690.83			Hg ₂ SO ₄ (c)	-177.72	-149.70	47.96 ^{164,165}
Hg ²⁺ (aq)	40.67 ⁵³	39.365 ⁵⁶	-8.6 ₆ ⁵⁶	HgSe(c)	-10.8 ¹⁴⁷	-9.1 ¹⁴⁷	22.5 ¹⁴⁷
Hg ³⁺ (g)	1480.			HgSeO ₃ (c)		-67.9 ^b	
Hg ₂ (g)	26.0	16.3	68.82	Hg ₂ SeO ₃ (c)		-71.1	
Hg ₂ ²⁺ (aq)	39.87 ⁵⁶	36.713 ⁵⁶	15.7 ₂ ⁵⁶	HgTe(c)	-8.1 ¹⁵⁰	-6.7 ¹⁵⁰	25.5 ¹⁵⁰
HgO(c, red, orthorh)	-21.71	-13.995	16.80 ⁵¹	Hg(N ₃) ⁺ (aq)		112.0 ²⁰⁴	
HgO(c, yellow, orthorh)	-21.71 ⁵³	-13.970 ⁵³	16.70 ⁵³	Hg(N ₃) ₂ (aq, undiss)		185.0 ²⁰⁴	
HgO(c, red, hexag)	-21.59 ⁵³	-13.940 ⁵³	17.0 ₃ ⁵³	Hg ₂ (N ₃) ₂ (c)	141.5 ²⁰⁶	178.4	49.9
HgO(g)			57.8 ⁸⁷	Hg(NO ₃) ⁺ (aq)		12.3 ²⁰³	
HgH(g)	57 ^{76,193}	51	52.50 ^{76,193}	Hg(NO ₃) ₂ (aq, undiss)		-12.0 ²⁰³	
Hg(OH) ⁺ (aq)	-20.2	-12.4 ₃ ^b	16.5	Hg(NO ₂) ₂ ²⁻ (aq)		-11.2 ²⁰¹	
Hg(OH) ₂ (aq, undiss)	-86.0	-65.6 ^b	30.2	Hg(NH ₃) ₂ ²⁺ (aq)		21.0 ¹⁹⁵	
Hg(OH) ₃ ⁻ (aq)		-102.1 ^c		Hg(NH ₃) ₂ ²⁺ (aq)	-22.6 ^b	2.8 ¹⁹⁵	41
HHgO ₂ ⁻ (aq)		-45.4 ^b		Hg(NH ₃) ₃ ²⁺ (aq)	-45.0 ^b	-4.9 ¹⁹⁵	62
HgF(g)	~0.7 ⁷⁶	~-4.4 ⁷⁶	59.34 ⁷⁶	Hg(NH ₃) ₄ ²⁺ (aq)	-67.8 ^b	-12.3 ¹⁹⁵	80
HgF ⁺ (aq)	-38.0 ^b	-29.4 ^b	-2 ^b	HgNH ₂ Br(c, orthorh)			31.83 ¹³¹
Hg ₂ F ₂ (c)	-116	-103 ⁷⁷	(40)	HgNH ₂ Br(c, cubic)			31.09 ¹³¹
HgCl(g)	20	15	62.1	Hg ₂ (P ₂ O ₇) ²⁻		-435.	
HgCl ⁺ (aq)	-4.7 ^b	-1.2 ^b	17 ^b	Hg ₂ (OH)(P ₂ O ₇) ³⁻		-481.	
HgCl ₂ (c)	-54.0	-43.1	34.9	Hg ₂ (P ₂ O ₇) ₂ ⁶⁻ (aq)		-883	
HgCl ₂ (g)	-34.2 ¹²⁴	-33.9 ¹²⁴	70.43 ^{76,124}	Hg ₂ (OH) ₂ (P ₂ O ₇) ⁴⁻		-525	
HgCl ₂ (aq, undiss)	-51.9 ^b	-41.3 ^b	36 ^b	Hg(C ₂ O ₄)(c)	-162.1		
HgCl ₃ ⁻ (aq)	-93.1 ^b	-73.8 ^b	49 ^b	Hg ₂ CO ₃ (c)	-132.3	-111.9	43.
HgCl ₄ ²⁻ (aq)	-132.6 ^b	-106.7 ^b	69 ^b	Hg ₂ (C ₂ O ₄)(c)		-141.8	
HgCl(OH)(aq, undiss)	-69.0 ¹¹⁸	-53.1 ^{118,119}	32	Hg ₂ (C ₂ O ₄) ₂ ²⁻ (aq)		-295.0	
Hg ₂ Cl ₂ (c)	-63.47 ₅ ^{56,86}	-50.376 ^{56,86}	45.7 ₅ ^{56,86}	Hg ₂ (OH)(C ₂ O ₄) ⁻		-179.8	
HgBr(g)	~25 ⁷⁶	~16 ⁷⁶	64.9 ⁷⁶	Hg(CH ₃)(g)	40.		
HgBr ⁺ (aq)	1.3 ^b	2.2 ^b	18 ^b	Hg(CH ₃) ₂ (liq)	14.3	33.5	50.
HgBr ₂ (c)	-40.8	-36.6	41.	Hg(CH ₃) ₂ (g)	22.56	34.9	73.
HgBr ₂ (g)	-20.7 ⁷⁶	-27.2 ⁷⁶	76.511 ⁷⁶	Hg(CH ₃)(C ₂ H ₅) (liq)	11.1		
HgBr ₂ (aq, undiss)	-38.6 ^b	-34.1 ^b	40 ^b	Hg(C ₂ H ₅) ₂ (liq)	7.2		
HgBr ₃ ⁻ (aq)	-70.3 ^b	-61.9 ^b	61 ^b	Hg(C ₂ H ₅) ₂ (g)	18.0		
HgBr ₄ ²⁻ (aq)	-103.2 ^b	-88.6 ^b	73 ^b	Hg biphenyl (c)	67.6 ²¹¹		
HgBr(OH)(aq, undiss)		-49.7 ¹²⁰		Hg ₂ Ac ₂ (c)	-201	-152.99	~74
HgBrCl(g)			71.55	(Ac ⁻ = ace- tate)			
HgBrCl(aq, undiss)		-38.6 ^b		Hg(CH ₃)Cl(c)	-27.8		
Hg ₂ Br ₂ (c)	-49.46	-43.280 ^{92,93}	52.0	Hg(CH ₃)Cl(g)	-12.5		
HgI(g)	31.6 ⁹⁹	21.9 ⁹⁹	67.26	Hg(C ₂ H ₅)Cl(c)	-33.3		
HgI ⁺ (aq)	10.1 ^b	9.6 ^b	18 ^b	Hg(C ₂ H ₅)Cl(g)	-15.0		
HgI ₂ (c, red)	-25.2	-24.3	43.	HgCl ₂ ·CH ₃ OH(c)	-113.5 ^d	-83.1 ^d	58.
HgI ₂ (c, yellow)	-24.6			HgCl ₂ ·2CH ₃ OH (c)	-172 ²⁴¹	-123.0 ²⁴¹	80 ²⁴¹
HgI ₂ (g)	-4.1	-14.3	80.31	Hg(CH ₃)Br(c)	-20.5		
HgI ₂ (aq, undiss)	-19.2 ^b	-17.9 ^b	41 ^b	Hg(CH ₃)Br(g)	-4.4		
HgI ₃ ⁻ (aq)	-36.7 ^b	-35.4 ^b	71 ^b	Hg(C ₂ H ₅)Br(c)	-25.5		
HgI ₄ ²⁻ (aq)	-56.4 ^b	-50.5 ^b	85 ^b	Hg(C ₂ H ₅)Br(g)	-7.2		
HgI(OH)(aq, undiss)		-41.4 ¹²¹		Hg(CH ₃)I(c)	-10.2		
HgICl(aq)		-30.7 ^b		Hg(CH ₃)I(g)	5.2		
HgIBr(g)			76.59	Hg(C ₂ H ₅)I(c)	-15.7		
HgIBr(aq, undiss)		-26.6 ^b		Hg(C ₂ H ₅)I(g)	3.3		
HgIBr ₃ ²⁻ (aq)		-80.47 ^b		Hg(CN) ⁺ (aq)	53.7 ^b	57.0 ^b	15.8
HgI ₂ Br ₂ ²⁻ (aq)		-71.08 ^b		Hg(CN)Cl(aq, undiss)		16.1 ¹⁷⁴	
HgI ₃ Br ₂ ⁻ (aq)		-61.1 ^b		Hg(CN)Br(aq, undiss)		20.1 ¹⁷⁴	
Hg ₂ I ₂ (c)	-29.00	-26.53	55.8				

TABLE Ia (Continued)

Substance	ΔH_f° , kcal mol ⁻¹	ΔG_f° , kcal mol ⁻¹	S° , cal K ⁻¹ mol ⁻¹	Substance	ΔH_f° , kcal mol ⁻¹	ΔG_f° , kcal mol ⁻¹	S° , cal K ⁻¹ mol ⁻¹
Hg(CN)I(aq, undiss)		29.0 ^{174,175}		Hg(SCN) ₃ ⁻ (aq)		78.8 ^{185,186}	
Hg(CN) ₂ (c)	66 ²⁰⁹			Hg(SCN) ₄ ²⁻ (aq)	77.8 ^b	98.4 ^{185,186}	108
Hg(CN) ₂ (g)	63.0			Hg(OH)(SCN) (aq, undiss)		110.4 ⁶⁵	
Hg(CN) ₂ (aq, undiss)	66.3 ^b	74.7 ^b	38.5	Hg(SCN)(CN) ₃ ²⁻		132.3 ^b	
Hg(CN) ₂ Cl ⁻ (aq)		43.7 ^b		Hg(SCN) ₂ (c)		54.1 ¹⁴¹	
Hg(CN) ₃ ⁻ (aq)	94.7 ^b	110.8 ^b	52.5	Hg(ma) ²⁺ (aq) (ma = methyl-amine)		32.5	
Hg(CN) ₃ Cl ²⁻ (aq)		80.		Hg(ma) ₂ ²⁺ (aq)	-13.3 ²²³	24.9	63.4
Hg(CN) ₃ Br ²⁻ (aq)		85.		HgCl(ma) ⁺ (aq)	-35.5 ²²³	-8.3	40.3
Hg(CN) ₂ (tu)(aq) (tu = thiourea)	49.3 ¹¹⁸			Hg(gl) ⁺ (aq) (gl ⁻ = gly-cinate)		-49.9 ^b	
Hg(CN) ₂ (tu) ₂ (aq)	25.1 ¹¹⁸			Hg(gl) ₂ (aq, undiss)	-205.6 ^b	-137.4 ^b	63 ^b
Hg(ONC) ₂ (c) (mercuric fulminate)	64.			HgCl(gl)(aq, undiss)	-130.3 ^b	-89.9 ^b	46 ^b
Hg(SCN) ⁺ (aq)		49.3 ^{185,186}		Hg(en) ₂ ²⁺ (aq) (en = ethylene-diamine)	-16.3 ^b		
Hg(SCN)Cl(aq, undiss)		8.5 ^b		HgCl(en) ⁺ (aq)	-33.9 ^b		
Hg(SCN)Br(aq, undiss)		12.3 ^b		Hg ₂ CrO ₄ (c)		-149.1 ¹⁴¹	
Hg(SCN) ₂ (aq, undiss)	46.7 ^b	60.5 ^{185,186}	36				

^a All values in italics are taken from NBS 270-4.²⁹ Estimated values are in parentheses. Superscript numbers on some quantities indicate references cited in the text; other quantities are discussed in the text, where references may be found. ^b Based on values tabulated in NBS 270-4, adjusted to take into account the new ΔH_f° and S° values for Hg²⁺(aq). ^c HHgO₂⁻(aq) and Hg(OH)₃⁻(aq) are merely different representations of the same species, with thermodynamic properties that differ by the value of the same property for H₂O(lig). ^d Based on values tabulated in NBS 270-4, adjusted to take into account our revised ΔH_f° and S° values for HgCl₂(c).

ous species of mercury. The relatively low stability of HgO as compared to many other metal oxides has an important bearing on stabilities and reactivities of many compounds of mercury.

Many mercury compounds are readily precipitated from aqueous solution. Soluble compounds are mostly rather weak electrolytes. Mercury(II) complexes are generally more stable than complexes of the same ligand with zinc, cadmium, or mercury(I) ions. Addition of complexing agents to Hg(I) compounds in aqueous systems often leads to disproportionation to Hg(liq) and Hg(II) complexes. But some stable Hg(I) complexes are known, as described later in this review.

It is now well known that many mercurous compounds contain discrete Hg₂²⁺ ions and that Hg₂²⁺(aq) ions are important in aqueous solutions. This knowledge has come from a variety of kinds of investigations, including X-ray crystallography, Raman spectra of solutions, magnetic susceptibilities, solution equilibria, and electrical conductivities.

Recent investigations have provided evidence for Hg₃²⁺ (formal +2/3 oxidation state) in AlCl₃-NaCl melts²⁶ and in SO₂(liq).²⁷ Preparation and structure of [Hg_{2.86}AsF₆] have also been described.²⁸ Other work on lower oxidation states of mercury is cited in these papers.²⁶⁻²⁸

Mercury forms a wide range of organometallic compounds that are of considerable importance in several respects. The effective stabilities of these compounds may be attributed to the considerable tendency of mercury to form covalent bonds and also to the relatively low stability of HgO.

III. Elementary Mercury

Our best general source of thermodynamic data for elementary mercury (also compounds and aqueous species) is the National Bureau of Standards Technical Note 270-4,²⁹ to which we frequently refer as NBS 270-4. Thermodynamic properties in NBS 270-4 are given in terms of kcal mol⁻¹ and

cal K⁻¹ mol⁻¹. All of our discussion of thermodynamic properties is in terms of these units. Because the scientific world is in the midst of a gradual change toward use of such units as kJ mol⁻¹ and J K⁻¹ mol⁻¹, we list thermodynamic properties in Table Ia in terms of calories (kcal mol⁻¹ and cal K⁻¹ mol⁻¹) and in Table Ib in terms of joules (kJ mol⁻¹ and J K⁻¹ mol⁻¹).

We follow NBS 270-4 in taking $\Delta G_f^\circ = 0$, $\Delta H_f^\circ = 0$, and $S^\circ = 18.17$ cal K⁻¹ mol⁻¹ for Hg(liq) at 298 K. This entropy is consistent with the heat capacities of Busey and Giauque³⁰ and Smith and Wolcott.³¹ We also note that Douglas, Ball, and Ginnings³² have measured ($H_T - H_{273}$) for Hg(liq) by a "drop" method over the range 0-450°C.

The NBS 270-4 lists $\Delta G_f^\circ = 7.613$ kcal mol⁻¹ for Hg(g) at 298 K. This value corresponds to a vapor pressure of 2×10^{-3} Torr, which is consistent with the results of many investigators.^{30,33-36} The NBS 270-4 $\Delta H_f^\circ = 14.655$ kcal mol⁻¹ for Hg(g) is consistent with the enthalpy of vaporization calculated by Busey and Giauque³⁰ from heat capacity and vapor pressure results that they have reviewed.

Vapor pressure measurements (260-360°C) by Spedding and Dye³³ are in good agreement with some previous results and with our tabulated thermodynamic properties. These authors make the old but often neglected point that equations fitted to experimental data must be used cautiously for extrapolation outside the range of measurement. Here it is appropriate to make the related point that several equations that fit the experimental results about equally well can lead to significantly different derivatives such as $d \ln P/dT$, as illustrated by the three equations presented by Spedding and Dye³³ that correspond to a spread of 33 cal mol⁻¹ in the calculated enthalpy of vaporization of Hg(liq) at 298 K.

The vapor pressure equation reported by Schmahl, Barthel, and Kaloff³⁵ corresponds to a slightly smaller vapor pressure and slightly larger enthalpy of vaporization at 298 K than do our tabulated thermodynamic properties of Hg(g).

TABLE Ib.^a Thermodynamic Properties of Mercury at 298 K

Substance	ΔH_f° , kJ mol ⁻¹	ΔG_f° , kJ mol ⁻¹	S° , J K ⁻¹ mol ⁻¹	Substance	ΔH_f° , kJ mol ⁻¹	ΔG_f° , kJ mol ⁻¹	S° , J K ⁻¹ mol ⁻¹
Hg(liq)	0	0	76.02 ^{30,31}	HgS(c, red)	-54.0	-46.4	82.4 ¹³⁶
Hg(g)	61.317	31.853	174.85	HgS(c, black)	-50.2	-44.4	88.7
Hg(aq)	13.93 ⁴³	37.2 ⁴³	-2.1	HgSO ₄ (c)	-707.5	-594	(142)
Hg ⁺ (g)	1074.53			HgSO ₄ (aq, undiss)		-587.9 ^b	
Hg ²⁺ (g)	2890.4			Hg ₂ SO ₄ (c)	-743.58	-626.34	200.66 ^{164,165}
Hg ²⁺ (aq)	170.16 ⁵³	164.703 ⁵⁶	-36.23 ⁵⁶	HgSe(c)	-45.2 ¹⁴⁷	-38.1 ¹⁴⁷	94.1 ¹⁴⁷
Hg ³⁺ (g)	6192			HgSeO ₃ (c)		-284.1 ^b	
Hg ₂ (g)	109	68.2	287.9	Hg ₂ SeO ₃		-297.5	
Hg ₂ ²⁺ (aq)	166.82 ⁵⁶	153.607 ⁵⁶	65.77 ⁵⁶	HgTe(c)	-33.9 ¹⁵⁰	-28.0 ¹⁵⁰	106.7 ¹⁵⁰
HgO(c, red, orthorh)	-90.83	-58.555	70.29 ⁵¹	Hg(N ₃) ⁺ (aq)		468.6 ²⁰⁴	
HgO(c, yellow, orthorh)	-90.83 ⁵³	-58.450 ⁵³	69.87 ⁵³	Hg(N ₃) ₂ (aq, undiss)		774.0 ²⁰⁴	
HgO(c, red, hexag)	-90.33 ⁵³	-58.325 ⁵³	71.25 ⁵³	Hg ₂ (N ₃) ₂ (c)	592.0 ²⁰⁶	746.4	208.8
HgO(g)			241.8 ⁸⁷	Hg(NO ₃) ⁺ (aq)		51.5 ²⁰³	
HgH(g)	238 ^{76,193}	213	219.7 ^{76,193}	Hg(NO ₃) ₂ (aq, undiss)		-50.2 ²⁰³	
Hg(OH) ⁺ (aq)	-84.5	-52.01 ^b	69.0	Hg(NO ₂) ₄ ²⁻ (aq)		-46.9 ²⁰¹	
Hg(OH) ₂ (aq, undiss)	-359.8	-274.5 ^b	126.4	Hg(NH ₃) ₂ ²⁺ (aq)		87.9 ¹⁹⁵	
Hg(OH) ₃ ⁻ (aq)		-427.2 ^c		Hg(NH ₃) ₂ ²⁺ (aq)	-94.6 ^b	11.7 ¹⁹⁵	172
HHgO ₂ ⁻ (aq)		-190.0 ^b		Hg(NH ₃) ₃ ²⁺ (aq)	-188.3 ^b	-20.5 ¹⁹⁵	259
HgF(g)	~2.9	~-18.4 ⁷⁶	248.28 ⁷⁶	Hg(NH ₃) ₄ ²⁺ (aq)	-283.7 ^b	-51.5 ¹⁹⁵	335
HgF ⁺ (aq)	-159.0 ^b	-123.0 ^b	-8 ^b	HgNH ₂ Br(c, orthorh)			133.18 ¹³¹
Hg ₂ F ₂ (c)	-485	-431 ⁷⁷	(167)	HgNH ₂ Br(c, cubic)			130.08 ¹³¹
HgCl(g)	83.7	62.8	259.9	Hg ₂ (P ₂ O ₇) ²⁻ (aq)		-1820	
HgCl ⁺ (aq)	-19.7 ^b	-5.0 ^b	71 ^b	Hg ₂ (OH)(P ₂ O ₇) ³⁻ (aq)		-2012	
HgCl ₂ (c)	-225.9	-180.3	146.0	Hg ₂ (P ₂ O ₇) ₂ ⁶⁻ (aq)		-3694	
HgCl ₂ (g)	-143.1 ¹²⁴	-141.8 ¹²⁴	294.68 ^{76,124}	Hg ₂ (OH) ₂ (P ₂ O ₇) ⁴⁻ (aq)		-2197	
HgCl ₂ (aq, undiss)	-217.1 ^b	-172.8 ^b	151 ^b	Hg(C ₂ O ₄)(c)	-678.2		
HgCl ₃ ⁻ (aq)	-389.5 ^b	-308.8 ^b	205 ^b	Hg ₂ CO ₃ (c)	-553.5	-468.2	180
HgCl ₄ ²⁻ (aq)	-554.8 ^b	-446.4 ^b	289 ^b	Hg ₂ (C ₂ O ₄)(c)		-593.3	
HgCl(OH)(aq, undiss)	-288.7 ¹¹⁸	-222.2 ^{118,119}	134	Hg ₂ (C ₂ O ₄) ₂ ²⁻ (aq)		-1234.3	
Hg ₂ Cl ₂ (c)	-265.579 ^{56,86}	-210.773 ^{56,86}	191.42 ^{56,86}	Hg ₂ (OH)(C ₂ O ₄) ⁻ (aq)		-752.3	
HgBr(g)	~105 ⁷⁶	~67 ⁷⁶	271.5 ⁷⁶	Hg(CH ₃)(g)	167		
HgBr ⁺ (aq)	5.4 ^b	9.2 ^b	75 ^b	Hg(CH ₃) ₂ (liq)	59.8	140.2	209
HgBr ₂ (c)	-170.7	-153.1	172	Hg(CH ₃) ₂ (g)	94.39	146.0	305
HgBr ₂ (g)	-86.6 ⁷⁶	-113.8 ⁷⁶	320.12 ⁷⁶	Hg(CH ₃)(C ₂ H ₅)(liq)	46.4		
HgBr ₂ (aq, undiss)	-161.5 ^b	-142.7	167 ^b	Hg(C ₂ H ₅) ₂ (liq)	30.1		
HgBr ₃ ⁻ (aq)	-294.1 ^b	-259.0 ^b	255 ^b	Hg(C ₂ H ₅) ₂ (g)	75.3		
HgBr ₄ ²⁻ (aq)	-431.8 ^b	-370.7 ^b	305 ^b	Hg biphenyl(c)	282.8 ²¹¹		
HgBr(OH)(aq, undiss)		-207.9 ¹²⁰		Hg ₂ Ac ₂ (c)	-841	-640.11	~310
HgBrCl(g)			299.4	(Ac ⁻ = acetate)			
HgBrCl(aq, undiss)		-161.5 ^b		Hg(CH ₃)Cl(c)	-116.3		
Hg ₂ Br ₂ (c)	-206.94	-181.084 ^{92,93}	217.6	Hg(CH ₃)Cl(g)	-52.3		
HgI(g)	132.2 ⁹⁹	91.6 ⁹⁹	281.42	Hg(C ₂ H ₅)Cl(c)	-139.3		
HgI ⁺ (aq)	42.3 ^b	40.2 ^b	75 ^b	Hg(C ₂ H ₅)Cl(g)	-62.8		
HgI ₂ (c, red)	-105.4	-101.7	180	HgCl ₂ ·CH ₃ OH(c)	-474.9 ^d	-347.7 ^d	243
HgI ₂ (c, yellow)	-102.9			HgCl ₂ ·2CH ₃ OH(c)	-720 ²⁴¹	-514.6 ²⁴¹	335 ²⁴¹
HgI ₃ (g)	-17.2	-59.8	336.02				
HgI ₂ (aq, undiss)	-80.3 ^b	-74.9 ^b	172 ^b				
HgI ₃ ⁻ (aq)	-153.6 ^b	-148.1 ^b	297 ^b				
HgI ₄ ²⁻ (aq)	-236.0 ^b	-211.3 ^b	356 ^b				
HgI(OH)(aq, undiss)		-173.2 ¹²¹					
HgICl(aq)		-128.4 ^b					
HgIBr(g)			320.45				
HgIBr(aq, undiss)		-111.3 ^b					
HgIBr ₃ ²⁻ (aq)		-336.69 ^b					
HgI ₂ Br ₂ ²⁻ (aq)		-297.40 ^b					
HgI ₃ Br ₂ ²⁻ (aq)		-255.6 ^b					
Hg ₂ I ₂ (c)	-121.34	-111.002	233.5				

TABLE Ib^a (Continued)

Substance	ΔH_f° , kJ mol ⁻¹	ΔG_f° , kJ mol ⁻¹	S° , J K ⁻¹ mol ⁻¹	Substance	ΔH_f° , kJ mol ⁻¹	ΔG_f° , kJ mol ⁻¹	S° , J K ⁻¹ mol ⁻¹
Hg(CH ₃)Br(c)	-85.8			Hg(SCN) ⁺ (aq)	206.3 ^{185,186}		
Hg(CH ₃)Br(g)	-18.4			Hg(SCN)Cl(aq, undiss)	35.6 ^b		
Hg(C ₂ H ₅)Br(c)	-106.7			Hg(SCN)Br (aq, undiss)	51.5 ^b		
Hg(C ₂ H ₅)Br(g)	-30.1			Hg(SCN) ₂ (aq, undiss)	195.4 ^b	253.1 ^{185,186}	151
Hg(CH ₃)I(c)	-42.7			Hg(SCN) ₃ ⁻ (aq)		329.7 ^{185,186}	
Hg(CH ₃)I(g)	21.8			Hg(SCN) ₄ ²⁻ (aq)	325.5 ^b	411.7 ^{185,186}	452
Hg(C ₂ H ₅)I(c)	-65.7			Hg(OH)(SCN) (aq, undiss)		461.9 ⁶⁵	
Hg(C ₂ H ₅)I(g)	13.8			Hg(SCN) (CN) ₃ ²⁻ (aq)		553.5 ^b	
Hg(CN) ⁺ (aq)	224.7 ^b	238.5 ^b	66.1	Hg ₂ (SCN) ₂ (c)		226.4 ¹⁴¹	
Hg(CN)Cl(aq, undiss)		67.4 ¹⁷⁴		Hg(ma) ²⁺ (aq) (ma = methylamine)		136.0	
Hg(CN)Br(aq, undiss)		84.1 ¹⁷⁴		Hg(ma) ₂ ²⁺ (aq)	-55.6 ²²³	104.2	265.3
Hg(CN)I(aq, undiss)		121.3 ^{174,175}		HgCl(ma) ⁺ (aq)	-148.5 ²²³	-34.7	168.6
Hg(CN) ₂ (c)	276 ²⁰⁹			Hg(gl) ⁺ (aq) (gl ⁻ = gly-cinate)		-208.8 ^b	
Hg(CN) ₂ (c)	263.6			Hg(gl) ₂ (aq, undiss)	-860.2 ^b	-574.9 ^b	264 ^b
Hg(CN) ₂ (g)	381			HgCl(gl)(aq, undiss)	-545.2 ^b	-376.1 ^b	192 ^b
Hg(CN) ₂ (aq, undiss)	277.4 ^b	312.5 ^b	161.1	Hg(en) ₂ ²⁺ (aq) (en = ethylene-diamine)	-68.2		
Hg(CN) ₂ Cl ⁻ (aq)		182.8 ^b		HgCl(en) ⁺ (aq)	-141.8 ^b		
Hg(CN) ₃ ⁻ (aq)	396.2 ^b	463.6 ^b	219.7	Hg ₂ CrO ₄ (c)		-623.8 ¹⁴¹	
Hg(CN) ₃ Cl ²⁻ (aq)		335					
Hg(CN) ₃ Br ²⁻ (aq)		356					
Hg(CN) ₂ (tu) (aq) (tu = thiourea)	206.3 ¹¹⁸						
Hg(CN) ₂ (tu) ₂ (aq)	105.0 ¹¹⁸						
Hg(ONC) ₂ (c) (mercuric fulminate)	268						

^a All values in italics are taken from NBS 270-4.²⁹ Estimated values are in parentheses. Superscript numbers on some quantities indicate references cited in the text; other quantities are discussed in the text, where references may be found. ^b Based on values tabulated in NBS 270-4, adjusted to take into account the new ΔH_f° and S° values for Hg²⁺(aq). ^c HgO₂⁺(aq) and Hg(OH)₃⁻(aq) are merely different representations of the same species, with thermodynamic properties that differ by the value of the same property for H₂O(lig). ^d Based on values tabulated in NBS 270-4, adjusted to take into account our revised ΔH_f° and S° values for HgCl₂(c).

Most recently, Ambrose and Sprake³⁶ have reported results of their extensive and very careful investigations of the vapor pressure of mercury, and have compared their results with those of earlier investigators. These recent results are also in agreement with our tabulated thermodynamic properties of Hg(lig) and Hg(g). It is possible that the higher temperature and pressure results might be used to obtain more information about Hg₂(g).

Hicks³⁴ has provided a review of vapor pressures and some related properties of mercury.

Hensel and Franck³⁷ have reported a metal-nonmetal transition in dense mercury vapor on the basis of their conductivity and density measurements that extend to 1700°C and 2100 bars.

Stallard, Rosenbaum, and Davis³⁸ have used an ultrasonic method for investigating thermal expansion and isothermal compressibility from 20 to 90°C and to 2000 bars. Grindley and Lind³⁹ have reported PVT data for mercury from 30 to 150°C and to 8000 bars.

The NBS 270-4 lists $\Delta G_f^\circ = 9.4$ kcal mol⁻¹ for Hg(aq), which corresponds to solubility of 1.3×10^{-7} *m*. Slightly larger solubilities (all about 2.9×10^{-7} *m*) have been reported by Moser and Voigt,⁴⁰ Choi and Tuck,⁴¹ Spencer and Voigt,⁴² and most recently by Glew and Hames.⁴³ This latter solubility⁴³ (2.9×10^{-7} *m*) corresponds to $\Delta G_f^\circ = 8.9$ kcal mol⁻¹ for Hg(aq), which is the value we adopt in Table I.

The $\Delta H_f^\circ = 9.0$ kcal mol⁻¹ for Hg(aq) listed in NBS 270-4

is slightly larger than the uncertain value we have calculated from the solubilities reported at different temperatures by Choi and Tuck.⁴¹ Spencer and Voigt⁴² have also measured solubilities at several temperatures and calculated $\Delta H^\circ = 5.1$ kcal mol⁻¹ for the enthalpy of solution and thence the same value for ΔH_f° of Hg(aq). Glew and Hames⁴³ have made what appears to be the "best" and is certainly the most extensive investigation of the solubility of mercury in water over a range of temperature. Their results lead to $\Delta H_f^\circ = 3.33$ kcal mol⁻¹ for Hg(aq). We adopt this value and the corresponding $S^\circ = -0.5$ cal K⁻¹ mol⁻¹ for Hg(aq) for our Table I, but caution that it is possible that other values^{29,41,42} might be better.

The ΔH_f° and S° values listed in NBS 270-4 for Hg(aq) are consistent with those estimated by "reasonable" extrapolation of similar properties of aqueous krypton and xenon² to atomic weight 201 g mol⁻¹. On the other hand, the results of Spencer and Voigt⁴² correspond to a larger enthalpy of vaporization from aqueous solution and a smaller entropy for Hg(aq) than estimated from properties² of monatomic noble gases. Finally, the results of Glew and Hames⁴³ correspond to a considerably greater enthalpy of vaporization and also a considerably smaller entropy for Hg(aq) than any of the values mentioned above. As pointed out by Glew and Hames,⁴³ who considered the problem from a somewhat different point of view, these thermodynamic properties are consistent with the idea that there is considerable "solvation"

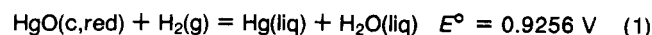
of the relatively polarizable Hg solute atoms. In connection with this interpretation it would be interesting to have solubility data at several pressures and thence the $\Delta \bar{V}^\circ$ of solution and the \bar{V}° of Hg(aq).⁴⁴

Glew and Hames⁴⁵ have determined the solubility of mercury in 6.10 M NaCl(aq) at several temperatures and have discussed their results in terms of salting out coefficients.

We also note that Kuntz and Mains⁴⁶ and Spencer and Voigt⁴⁷ have investigated solubilities of mercury in a number of organic solvents. Rosenberg and Kay⁴⁸ have measured solubilities of mercury in polar gases from 220 to 300°C and at pressures up to 30 atm.

IV. Mercuric Oxide

The NBS 270-4 lists $\Delta G_f^\circ = -13.995 \text{ kcal mol}^{-1}$ for HgO(c, red, orthorhombic). This value is consistent with the oxygen decomposition pressure measurements of Taylor and Hulett⁴⁹ and is also supported by electrochemical results as follows. The NBS tabulated^{2,29} free energies lead to the cell potential:



Results of several sets of cell measurements^{50,51} are in very good agreement with this potential and thence with the ΔG_f° of HgO(c,red). The NBS tabulated^{2,29} free energies also lead to the cell potential:



Measurements by Hamer and Craig⁵⁰ and by Gregor and Pitzer⁵² have led to slightly smaller values for this potential, corresponding to standard free energies of reaction that differ by only 0.06 and 0.03 kcal mol⁻¹ from the ΔG° calculated from tabulated^{2,29} ΔG_f° values. Because most of this small discrepancy can be attributed to experimental difficulties and related uncertainties in the ΔG_f° of Ag₂O(c), we may regard this ΔG_f° of HgO(c,red,orthorhombic) as being well established.

Vanderzee, Rodenburg, and Berg⁵³ have reviewed structural and solubility investigations of HgO(c,red,orthorhombic) in relation to HgO(c,yellow,orthorhombic) and HgO(c,red,hexagonal). We adopt in Table I the ΔG_f° values they have recommended for these latter two forms of mercuric oxide.

The NBS 270-4 lists $S^\circ = 16.80 \text{ cal K}^{-1} \text{ mol}^{-1}$ for HgO(c,red,orthorhombic), which is the value reported by Bauer and Johnston⁵¹ on the basis of their heat capacities. Bauer and Johnston⁵¹ have cited Randall's calculations with decomposition pressure data⁴⁹ with results that now lead us to $S^\circ = 17.0 \text{ cal K}^{-1} \text{ mol}^{-1}$ for HgO(c,red,orthorhombic). Hamer and Craig⁵⁰ have reviewed a considerable number of electrochemical investigations of the reaction represented by eq 1. Accepting the "best" dE°/dT and derived ΔS° from their review, we now calculate $S^\circ = 17.0 \text{ cal K}^{-1} \text{ mol}^{-1}$ for HgO(c,red,orthorhombic). Other dE°/dT values cited by Hamer and Craig⁵⁰ are consistent with S° values as large as 17.3 and as small as 16.6 cal K⁻¹ mol⁻¹ for HgO(c,red,orthorhombic). The dE°/dT values for the cell represented by eq 2 as investigated by Hamer and Craig⁵⁰ and by Gregor and Pitzer⁵² lead to $S^\circ = 17.6 \text{ cal K}^{-1} \text{ mol}^{-1}$ for HgO(c,red,orthorhombic). Gregor and Pitzer⁵² also suggested that a different treatment of the low temperature heat capacity data⁵¹ would lead to $S^\circ > 16.8 \text{ cal K}^{-1} \text{ mol}^{-1}$ for HgO(c,red,orthorhombic). On the basis of all of these values, it is reasonable to accept $S^\circ = 16.8 \text{ cal K}^{-1} \text{ mol}^{-1}$ for HgO(c,red,orthorhombic) as listed in NBS 270-4, but it should be noted that there is some evidence for a larger entropy.

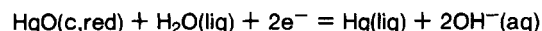
Combination of the NBS tabulated^{2,29} ΔG_f° and S° values leads to the $\Delta H_f^\circ = -21.71 \text{ kcal mol}^{-1}$ listed in NBS 270-4 for HgO(c,red,orthorhombic). If we had taken a slightly larger

S° as "best" for mercuric oxide, we would obtain a slightly less exothermic ΔH_f° . Bichowsky and Rossini⁵⁴ calculated $\Delta H_f^\circ = -21.3 \text{ kcal mol}^{-1}$ from results of older calorimetric measurements, but adopted $\Delta H_f^\circ = -21.6 \text{ kcal mol}^{-1}$ based on decomposition pressures and dE°/dT results. We now conclude that it is reasonable to accept $\Delta H_f^\circ = -21.71 \text{ kcal mol}^{-1}$ for HgO(c,red,orthorhombic) as tabulated in NBS 270-4, while noting that there is some evidence for a less exothermic value. Although uncertainties in the thermodynamic properties of HgO(c,red,orthorhombic) are not large, they are still significant because these properties are used in evaluating corresponding properties of Hg²⁺(aq) and thence the properties of many other species. Further investigations of this compound may be worthwhile.

Along with their review of solubilities, Vanderzee, Rodenburg, and Berg⁵³ have made calorimetric measurements leading to the ΔH_f° and S° values for HgO(c,yellow,orthorhombic) and HgO(c,red,hexagonal) that we list in Table I.

On the basis of $\Delta C_p^\circ \approx 0$ for transformation of one form of HgO(c) to another, we calculate that the red orthorhombic form is more stable than the yellow form at all temperatures, but becomes less stable than the red hexagonal form at ~520 K. The tabulated thermodynamic properties also indicate that the yellow form is more stable than the red hexagonal form up to ~360 K. Heat capacity and possibly DTA measurements above 298 K could be useful in connection with understanding relationships between the various forms of HgO(c) and also in connection with thermodynamic calculations based on high-temperature decomposition pressures as discussed earlier in this section.

We use our adopted ΔG_f° for HgO(c,red,orthorhombic) to calculate the following standard potential:



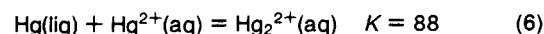
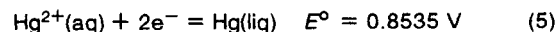
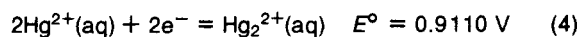
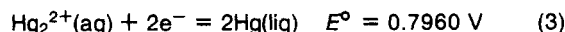
$$E^\circ = 0.0977 \text{ V}$$

The HgO|Hg electrode corresponding to the half-reaction above has proven useful in investigations of alkaline solutions. Thacker⁵⁵ has described a simple preparation of this electrode.

We consider the solubility of HgO(c) in the next section, following our discussion of the thermodynamic properties of Hg₂²⁺(aq) and Hg²⁺(aq).

V. Hg₂²⁺(aq), Hg²⁺(aq), and Hydrolyzed Species

For both Hg₂²⁺(aq) and Hg²⁺(aq) we adopt the ΔG_f° values calculated by Vanderzee and Swanson⁵⁶ from results of a number of electrochemical investigations that they have thoroughly reviewed. These free energies lead to the following standard potentials and equilibrium constant:

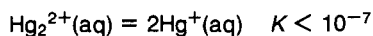


In addition to the experimental results already cited⁵⁶ in support of these values, we note that McKeown⁵⁷ has found $K = 90$ for equilibrium 6, in excellent agreement with the value above.

Zielen and Sullivan⁵⁸ have carried out measurements on the Hg₂²⁺|Hg and Hg²⁺|Hg₂²⁺ couples at 25°C in 2.0 M perchlorate media and have reached conclusions that are of general importance with respect to application of the principle of constant ionic strength.

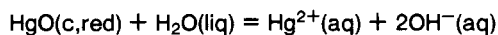
Moser and Voigt⁴⁰ have discussed previous work and set a

limit on possible dissociation of aqueous mercurous ions as indicated by



It might be possible to detect $\text{Hg}^+(\text{aq})$ ions by esr measurements on mercurous perchlorate solutions.

The tabulated ΔG_f° values for $\text{HgO}(\text{c,red})$ and $\text{Hg}_2^{2+}(\text{aq})$ lead to the solubility product:



$$K_{\text{sp}} = 2.8 \times 10^{-26}$$

This K_{sp} value is in good agreement with that reported by Feitknecht and Schindler⁵⁹ and also cited in other useful reviews. Because these cited K_{sp} values have been calculated from potentials previously discussed here and by Vanderzee and Swanson,⁵⁶ they do not provide independent support for the tabulated thermodynamic quantities. We do, however, have solubility results that are independent of the various potentials. For example, from the solubility measurements of Garret et al.⁶⁰ we have $K_{\text{sp}} = 0.53 \times 10^{-26}$. The difference between this K_{sp} and the calculated value above corresponds to a total discrepancy of $1.0 \text{ kcal mol}^{-1}$ in ΔG_f° values for $\text{HgO}(\text{c,red})$ and $\text{Hg}_2^{2+}(\text{aq})$. Although there are only small uncertainties associated with the measured solubilities, there is substantial uncertainty associated with interpretation⁶⁰ in terms of $\text{Hg}_2^{2+}(\text{aq})$, $\text{Hg}(\text{OH})^+(\text{aq})$, etc. Thus it is reasonable to accept the calculated $K_{\text{sp}} = 2.8 \times 10^{-26}$ as the "best" value and to regard the quoted K_{sp} from solubilities as providing approximate confirmation of the tabulated free energies of $\text{HgO}(\text{c,red})$ and $\text{Hg}_2^{2+}(\text{aq})$.

We also have $\text{p}K_{\text{sp}} = 26.0$ (3 M ClO_4^-) from the work of Dyrssen and Tyrrell.⁶¹ In the absence of activity coefficients for this system, all we can say now is that this value is reasonable in relation to our calculated K_{sp} .

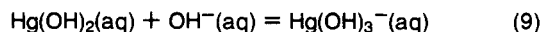
For hydrolyzed species of $\text{Hg}(\text{II})$ we adopt the following equilibrium constants and also the ΔG_f° values listed in Table I:



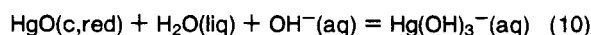
$$K = 2.6 \times 10^{-4}$$



$$K = 2.6 \times 10^{-3}$$



$$K = 0.16$$



$$K = 3.0 \times 10^{-5}$$

These equilibrium constants are consistent with the ΔG_f° values in NBS 270-4, but our tabulated ΔG_f° values are slightly different from theirs because our ΔG_f° for $\text{Hg}_2^{2+}(\text{aq})$ differs from theirs. It should also be recognized that $\text{Hg}(\text{O}-\text{H})_3^-(\text{aq})$ (as above) and $\text{HHgO}_2^-(\text{aq})$ (as in NBS 270-4) are merely different representations of the same species. The equilibrium constants above are in generally satisfactory agreement with the results of several investigations⁶⁰⁻⁶⁶ of the solubility of $\text{HgO}(\text{c,red})$ and hydrolysis of $\text{Hg}(\text{II})$ solutions.

Johansson's⁶⁷ X-ray investigations of aqueous $\text{Hg}(\text{ClO}_4)_2$ solutions (3.5 to 4.6 M) indicate that mercuric ions in acidic solution are coordinated to about six water molecules at approximately equal distances. Hydrolysis leads to shortening of the $\text{Hg}-\text{O}$ distance. There is X-ray evidence for polynuclear species, which have also been invoked by Ahlberg⁶² in interpretation of hydrolysis data.

We now turn to consideration of ΔH_f° and S° values for

the aqueous species whose free energies have been discussed above.

For $\text{Hg}_2^{2+}(\text{aq})$ we adopt $\Delta H_f^\circ = 40.67 \text{ kcal mol}^{-1}$ from the calorimetric ΔH° of solution of $\text{HgO}(\text{c,red})$ in $\text{HClO}_4(\text{aq})$ measured by Vanderzee, Rodenburg, and Berg.⁵³ Similar measurements by earlier investigators^{68,69} lead to a ΔH_f° value (identical with that listed in NBS 270-4) that is $0.2 \text{ kcal mol}^{-1}$ more endothermic than our adopted value. Combination of our adopted ΔH_f° with the ΔG_f° cited previously⁵⁶ leads to $S^\circ = -8.66 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2^{2+}(\text{aq})$ as also calculated by Vanderzee and Swanson.⁵⁶

For $\text{Hg}_2^{2+}(\text{aq})$ we adopt $\Delta H_f^\circ = 39.87 \text{ kcal mol}^{-1}$ and $S^\circ = 15.72 \text{ cal K}^{-1} \text{ mol}^{-1}$ as listed by Vanderzee and Swanson.⁵⁶ Their primary approach to these quantities involved combination of their calorimetrically measured enthalpy of precipitation of $\text{Hg}_2\text{Cl}_2(\text{c})$ with the ΔH_f° of $\text{Hg}_2\text{Cl}_2(\text{c})$ that we consider in the next section. Vanderzee and Swanson⁵⁶ have also combined their S° for $\text{Hg}_2^{2+}(\text{aq})$ with the ΔS° for reaction 6 that they have derived from the results of Schwarzenbach and Anderegg⁷⁰ to obtain a value of S° for $\text{Hg}_2^{2+}(\text{aq})$ that is very close to the adopted value.

There are several other paths to ΔH_f° and S° of $\text{Hg}_2^{2+}(\text{aq})$. For example, measurements by McKeown⁵⁷ lead to ΔS° for reaction 6 and thence to $S^\circ = 16.4 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2^{2+}(\text{aq})$. We also use the potentials ($20-35^\circ\text{C}$) reported by Pan, Chang, and Hsin⁷¹ for the couple represented by (3) to calculate $S^\circ = 13.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2^{2+}(\text{aq})$. Results obtained by Galloway⁷² and Read⁷³ for ΔS° of dissolution of $\text{Hg}_2\text{Cl}_2(\text{c})$ and $\text{Hg}_2\text{Br}_2(\text{c})$ as discussed in the next section of this review lead to $S^\circ = 17$ and $18 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2^{2+}(\text{aq})$. Using data on the solubility of $\text{Hg}_2\text{SO}_4(\text{c})$ from Sharma and Prasad⁷⁴ as discussed in section IX, we obtain $S^\circ = 20 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2^{2+}(\text{aq})$, which is the same as the value listed in NBS 270-4.

There are ΔH° and ΔS° values for hydrolysis of $\text{Hg}_2^{2+}(\text{aq})$ from the $\ln K/dT$ results of Anderegg et al.⁶⁴ and from the calorimetric results (3 M ClO_4^-) of Arnek and Kakolowicz.⁷⁵ We combine these quantities with our estimates of enthalpies of dilution to obtain the ΔH_f° and S° values listed in Table I for $\text{Hg}(\text{OH})^+(\text{aq})$ and $\text{Hg}(\text{OH})_2(\text{aq,undissociated})$. There are also enthalpy data (3 M ClO_4^-) available⁷⁵ for $\text{Hg}_2(\text{OH})^{3+}(\text{aq})$ and $\text{Hg}_2(\text{OH})_2^{2+}(\text{aq})$. Both of these species and also $\text{Hg}_4(\text{O}-\text{H})_3^{5+}(\text{aq})$ were postulated by Ahlberg⁶² in connection with equilibrium studies.

VI. Mercury(I) Halides

For $\text{HgF}(\text{g})$ we adopt the thermodynamic properties listed in the JANAF tables.⁷⁶ The S° is calculated from molecular constants and the ΔH_f° from the dissociation energy. It appears that the S° listed in NBS 270-4 is a mistake, leading to a corresponding error in the ΔG_f° for this compound.

For $\text{Hg}_2\text{F}_2(\text{c})$ we have $\Delta G_f^\circ = -102.2 \text{ kcal mol}^{-1}$ from the JANAF tables,⁷⁶ based on cell measurements of Koerber and DeVries,⁷⁷ and $\Delta G_f^\circ = -104.1 \text{ kcal mol}^{-1}$ from NBS 270-4, possibly based on the same measurements. On the basis of these values and our assessment of the cell results,⁷⁷ we take $\Delta G_f^\circ = -103 \text{ kcal mol}^{-1}$ and combine with our estimated $S^\circ = (40) \text{ cal K}^{-1} \text{ mol}^{-1}$ to obtain $\Delta H_f^\circ = -116 \text{ kcal mol}^{-1}$ for $\text{Hg}_2\text{F}_2(\text{c})$.

Combination of the NBS 270-4 ΔG_f° for $\text{Hg}_2\text{Cl}_2(\text{c})$ with the ΔG_f° for $\text{Cl}^-(\text{aq})$ ² leads to $E^\circ = 0.26814 \text{ V}$ for the $\text{Hg}_2\text{Cl}_2/\text{Hg}$ couple. This calculated potential is in good agreement with the reported results of a considerable number of careful investigations.⁷⁸⁻⁸⁵ Ahluwalia and Cobble⁸⁶ and Vanderzee and Swanson⁵⁶ have analyzed many of these results and have chosen $E^\circ = 0.268155 \text{ V}$. On the basis of these analyses and our own recalculations, we adopt the following potential:



This potential corresponds to $\Delta G_f^\circ = -50.376 \text{ kcal mol}^{-1}$ for $\text{Hg}_2\text{Cl}_2(\text{c})$ and is the value adopted for Table I.

We use the $\text{Hg}_2\text{Cl}_2|\text{Hg}$ potential above with the $\text{Hg}_2^{2+}|\text{Hg}$ potential given earlier to calculate the solubility product:



Most K_{sp} values quoted in the literature for $\text{Hg}_2\text{Cl}_2(\text{c})$ are derived from potentials (or related free energies) as outlined above and therefore are not a meaningful check on this value. But Galloway⁷² has made independent measurements that lead to $K_{\text{sp}} = 1.49 \times 10^{-18}$. The good agreement between this "direct" value and that derived from E° values (or related ΔG_f° values) offers convincing confirmation of the various tabulated free energies.

The only low-temperature heat capacity data available for $\text{Hg}_2\text{Cl}_2(\text{c})$ are the old (1911 and 1913) results of Pollitzer that have led Kelley and King⁸⁷ to $S^\circ = 46.0 \pm 0.5 \text{ cal K}^{-1} \text{ mol}^{-1}$ for this compound at 298.15 K. In the absence of modern thermal measurements, we must turn to dE°/dT results for the calomel electrode to obtain the "best" ΔH_f° and S° for $\text{Hg}_2\text{Cl}_2(\text{c})$ as described below.

Ahluwalia and Cobble⁶⁶ and Vanderzee and Swanson⁵⁶ have analyzed E° values at several temperatures in terms of the cell reaction



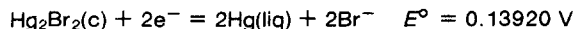
Both analyses are in agreement with $\Delta H^\circ = -16.429 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = -13.62 \text{ cal K}^{-1} \text{ mol}^{-1}$ for this reaction. We have repeated these analyses (using slightly different heat capacities) and have applied the same method of analysis to all other available results (generally of lower accuracy than those previously analyzed^{56,86}) and are now in agreement with the ΔH° and ΔS° values quoted above. These values lead us to $\Delta H_f^\circ = -63.47_5 \text{ kcal mol}^{-1}$ and $S^\circ = 45.7_5 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2\text{Cl}_2(\text{c})$ as listed in Table I. This ΔH_f° was used by Vanderzee and Swanson⁵⁶ in their evaluation of the thermodynamic properties of $\text{Hg}_2^{2+}(\text{aq})$.

Galloway's⁷² K_{sp} values for $\text{Hg}_2\text{Cl}_2(\text{c})$ at seven temperatures (15–45°C) lead to ΔH° and ΔS° values that are in reasonable agreement with ΔH_f° and S° values we have assigned to $\text{Hg}_2\text{Cl}_2(\text{c})$ and $\text{Hg}_2^{2+}(\text{aq})$.

We emphasize that a third law entropy of $\text{Hg}_2\text{Cl}_2(\text{c})$ would be useful.

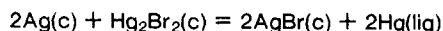
Calomel electrode measurements have been made in various salt solutions,⁸⁸ in several water-organic solvent mixtures,⁸⁹ and in formamide.⁹⁰ There have also been several investigations of Hg_2Cl_2 and other mercurous halides in molten salts.⁹¹

The free energies in NBS 270-4 and NBS 270-3 lead to $E^\circ = 0.13924 \text{ V}$ for the $\text{Hg}_2\text{Br}_2|\text{Hg}$ potential. On the basis of an average of the results of Gupta, Hills, and Ives⁹² and Leuschke and Schwabe⁹³ (recalculated using our E° for $\text{Hg}_2\text{Cl}_2|\text{Hg}$), we adopt the following:



This potential corresponds [using ΔG_f° for $\text{Br}^-(\text{aq})$ from NBS 270-3] to $\Delta G_f^\circ = -43.280 \text{ kcal mol}^{-1}$ for $\text{Hg}_2\text{Br}_2(\text{c})$ as in Table I.

We also note that Dakin and Ewing⁹⁴ and Larson⁹⁵ have measured potentials of cells in which the reaction is



and obtained $E^\circ = 0.06804$ and 0.06835 V , respectively. Combination of these potentials with ΔG_f° for $\text{AgBr}(\text{c})$ in NBS 270-4 leads to $E^\circ = 0.1413$ and 0.1416 V , respectively, for the $\text{Hg}_2\text{Br}_2|\text{Hg}$ potential. But we can also combine these mea-

sured potentials with $E^\circ = 0.07106 \text{ V}$ for $\text{AgBr}|\text{Ag}$ from Hetzer, Robinson, and Bates⁹⁶ to obtain $E^\circ = 0.1391$ and 0.1394 V , respectively, in better agreement with our adopted value.

We use our free energies to calculate the solubility product:



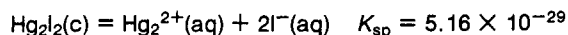
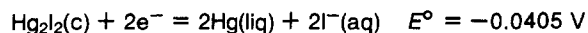
Several previously tabulated solubility products for $\text{Hg}_2\text{Br}_2(\text{c})$ have been calculated from ΔG_f° values or potentials similar to those cited above and do not constitute an independent check on our K_{sp} . But Read⁷³ has independently found $K_{\text{sp}} = 6.43 \times 10^{-23}$, which is in satisfactory agreement with our value.

The NBS 270-4 and Kelley and King⁸⁷ list $S^\circ = 52$ and $52.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, respectively, for $\text{Hg}_2\text{Br}_2(\text{c})$. On the basis of these values and results of our calculations with the temperature coefficients of Gupta, Hills, and Ives,⁹² Dakin and Ewing,⁹⁴ and Read,⁷³ we adopt $S^\circ = 52.0 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2\text{Br}_2(\text{c})$. The results of Larson⁹⁵ are in poor agreement with this value. Again we note that it would be useful to have a reliable entropy based on modern thermal measurements.

We combine our ΔG_f° and S° for $\text{Hg}_2\text{Br}_2(\text{c})$ to obtain the ΔH_f° that we list in Table I.

The $\text{Hg}_2\text{Br}_2|\text{Hg}$ electrode has been investigated⁹⁷ in aqueous alcohol systems.

The NBS 270-4 and NBS 270-3 free energies lead to the following potential and solubility product:



These values are consistent with the cell data of Bates and Vosburgh.⁹⁸ The ΔH_f° for $\text{Hg}_2\text{I}_2(\text{c})$ listed in NBS 270-4 is consistent with the results of older calorimetric and electrochemical results that have been reviewed by Bichowsky and Rossini⁵⁴ and in the JANAF tables.⁷⁶ The substantial uncertainties in these latter values could be considerably reduced by a third law entropy for $\text{Hg}_2\text{I}_2(\text{c})$.

For $\text{HgCl}(\text{g})$ we have thermodynamic properties listed in NBS 270-4 and the JANAF tables⁷⁶ that are in reasonable agreement. The properties of $\text{HgI}(\text{g})$ that are listed in NBS 270-4 have been revised in NBS 270-7,⁹⁹ with these latter values in agreement with those listed in the JANAF tables.⁷⁶ For $\text{HgBr}(\text{g})$ we have approximate ΔH_f° and ΔG_f° values and a more accurate S° from the JANAF tables.⁷⁶ Entropies for these $\text{HgX}(\text{g})$ compounds are also given by Kelley and King.⁸⁷ All of the ΔH_f° values are derived from dissociation energies and all of the entropies are calculated from molecular constants.

VII. Mercury(II) Halides

The ΔG_f° values for aqueous mercuric halide species listed in NBS 270-4 in combination with ΔG_f° values for the aqueous halide ions listed in NBS 270-3 lead to the equilibrium constants that are listed in Table II. The equilibria to which these equilibrium constants apply have been investigated many times by a variety of methods, often in perchlorate media ranging from 0.5 to 3.0 *M* so that there are some uncertainties in obtaining the "infinite dilution" equilibrium constants that we list. Nevertheless, the tabulated free energies (also ΔH_f° and S° values) are in generally reasonable agreement with experimental results of several workers,^{100–112} who provide references to earlier investigations.

We also note that Clarke and Woodward¹¹³ have presented spectroscopic evidence for existence of $\text{Hg}_2^{3+}(\text{aq})$ in moderately concentrated solutions.

The NBS 270-4 ΔG_f° values lead to a number of equilibri-

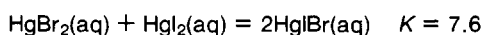
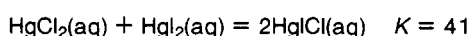
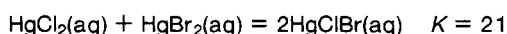
TABLE II. Equilibrium Constants at 298 K for Mercuric Halide Complexes

Reaction	K			
	F ⁻	Cl ⁻	Br ⁻	I ⁻
Hg ²⁺ (aq) + X ⁻ (aq) = HgX ⁺ (aq)	38	5.8 × 10 ⁶	1.1 × 10 ⁹	6.4 × 10 ¹²
HgX ⁺ (aq) + X ⁻ (aq) = HgX ₂ (aq)		2.5 × 10 ⁶	2.5 × 10 ⁸	1.3 × 10 ¹¹
HgX ₂ (aq) + X ⁻ (aq) = HgX ₃ ⁻ (aq)		6.7	1.5 × 10 ²	6.2 × 10 ³
HgX ₃ ⁻ (aq) + X ⁻ (aq) = HgX ₄ ²⁻ (aq)		13	23	1.1 × 10 ²
Hg ²⁺ (aq) + 4X ⁻ (aq) = HgX ₄ ²⁻ (aq)		1.3 × 10 ¹⁵	9.2 × 10 ²⁰	5.6 × 10 ²⁹

TABLE III. Equilibrium Constants at 298 K for HgBr₄²⁻(aq) + nI⁻(aq) = HgBr_{4-n}I_n²⁻(aq) + nBr⁻(aq)

n	K	n	K
1	1.6 × 10 ³	3	2.4 × 10 ⁷
2	3.1 × 10 ⁵	4	6.0 × 10 ⁸

um constants involving mixed halides in aqueous solution. Three of these follow:

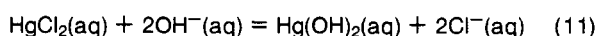


These values are in fair agreement with those reported by Marcus¹¹⁴ and Spiro and Hume.¹¹⁵ All of the above equilibrium constants are significantly greater than the statistical value of 4.

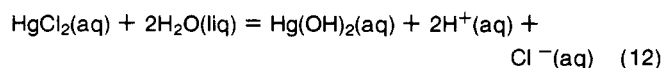
The NBS 270-4 ΔG_f° values also lead to the equilibrium constants for successive substitution of I⁻ for Br⁻ in HgBr₄²⁻(aq), as summarized in Table III. All four of these equilibrium constants are in excellent agreement with the results of Spiro and Hume¹¹⁶ for these reactions. Also, the equilibrium constant for $n = 4$ is in excellent agreement with independently determined stability constants for HgBr₄²⁻(aq) and HgI₄²⁻(aq).

We are unable to reconcile the unclear $d \ln K/dT$ results reported by Eliezer¹¹⁷ for mixed halides with NBS 270-4 ΔH_f° and S° values so our listings in Table I are limited to ΔG_f° values for these mixed halide species.

The NBS 270-4 and NBS 270-3 ΔG_f° values permit us to calculate $K = 5 \times 10^8$ for



and $K = 5 \times 10^{-20}$ for



The first equilibrium constant is larger than $K = 7.2 \times 10^7$ reported by Partridge, Izatt, and Christensen¹¹⁸ and the second is larger than $K = 2.5 \times 10^{-20}$ for 1 M ClO₄⁻ solution reported by Ciavatta and Grimaldi.¹¹⁹ Although these discrepancies are not huge, they are larger than uncertainties reported by these^{118,119} investigators and others already cited in connection with the properties of HgCl₂(aq) and Hg(OH)₂(aq). We retain the ΔG_f° values listed in Table I as previously listed in NBS 270-4 for these species, but note that some revisions might be advisable. It appears that uncertainties and possibly errors in reported properties are larger for Hg(OH)₂(aq) than for HgCl₂(aq).

Results of both groups^{118,119} cited above are in good agreement with $K = 1.2 \times 10^4$ for



We use this K value in calculating the ΔG_f° for HgCl(OH)(aq) listed in our Table I. Because of discrepancies noted above, this ΔG_f° may not have quite the right relationship to that tabulated for Hg(OH)₂(aq).

The ΔH_f° values in NBS 270-4 and NBS 270-3 lead to a calculated $\Delta H^\circ = -3.2 \text{ kcal mol}^{-1}$ for reaction 11, while the calorimetric measurements of Partridge, Izatt, and Christensen¹¹⁸ have led to $\Delta H^\circ = -2.5 \text{ kcal mol}^{-1}$. Because of uncertainties in all of the properties of these aqueous species, we do not feel it is appropriate to change from the NBS 270-4 ΔH_f° values [except as required because of our changed properties of Hg²⁺(aq)]. But we do use the results of Partridge, Izatt, and Christensen¹¹⁸ for reaction 13 for calculation of both ΔH_f° and S° of HgCl(OH)(aq). Because of discrepancies noted above, these values may not have quite the right relationship to those for Hg(OH)₂(aq).

Ahlberg and Leden¹²⁰ have investigated the equilibrium



in 3 and 0.5 M ClO₄⁻(aq) solution and have reported $K = 7.9 \times 10^5$ and $K = 4.8 \times 10^5$ for these solutions. Similarly, Ahlberg¹²¹ has found $K = 7.9 \times 10^8$ for



in 0.5 M ClO₄⁻(aq) solution. Our ΔG_f° values for HgBr(OH)(aq) and HgI(OH)(aq) are based on these results.^{120,121}

We also call attention to investigations of mercuric halide complexes in DMSO¹²² and in acetonitrile,¹²³ with the latter investigation including evaluation of the Hg²⁺|Hg₂²⁺ and Hg₂²⁺|Hg potentials and the equilibrium constant for disproportionation of Hg₂²⁺ in this solvent.

Johnson, Silva, and Cubicciotti¹²⁴ have made extensive measurements of the vapor pressure of HgCl₂(liq) from 573 K (vp = 0.96 atm) to 968 K (vp = 111.6 atm; critical temperature is 972 K). In a subsequent paper, Cubicciotti, Eding, and Johnson¹²⁵ reported results of their high-temperature calorimetric measurements on HgCl₂. These papers, which are admirable examples of high quality measurements and full thermodynamic treatment of resulting data, are a reliable source of ΔH°_{298} and ΔS°_{298} of vaporization of HgCl₂(c). Combining their quoted $S^\circ_{298} = 70.43 \text{ cal K}^{-1} \text{ mol}^{-1}$ for HgCl₂(g) (calculated from molecular constants) with their ΔS°_{298} of vaporization leads to $S^\circ_{298} = 34.9 \text{ cal K}^{-1} \text{ mol}^{-1}$ for HgCl₂(c), which is the value listed in NBS 270-4 and our Table I. It would be interesting to check this value against the results of modern heat capacity measurements and a third law entropy.

The $\Delta H_f^\circ = -53.6 \text{ kcal mol}^{-1}$ for HgCl₂(c) listed in NBS 270-4 is consistent with old enthalpy of reaction data⁵⁴ and our adopted ΔH_f° of Hg₂Cl₂(c). Combination of this ΔH_f° and the S° cited above leads to the NBS 270-4 $\Delta G_f^\circ = -42.7 \text{ kcal mol}^{-1}$ for HgCl₂(c). There are two other routes to ΔH_f° and ΔG_f° of HgCl₂(c), which we now consider.

Calculations with equilibrium constants given in Table II show that mercuric chloride in saturated solution (0.26–0.27 m at 25°C^{126,127}) exists primarily as HgCl₂(aq) with much smaller concentrations of other species such as HgCl⁺(aq), etc. Taking the activity coefficient of HgCl₂(aq) to be unity in combination with the solubility and the previously adopted ΔG_f° of HgCl₂(aq) leads us to $\Delta G_f^\circ = -42.2 \text{ kcal mol}^{-1}$ for HgCl₂(c). Combination of this value with the entropy then leads to $\Delta H_f^\circ = -53.1 \text{ kcal mol}^{-1}$ for HgCl₂(c).

Still another path involves the enthalpy of solution of $\text{HgCl}_2(\text{c})$ reported by Abraham, Irving, and Johnston¹²⁸ in combination with the tabulated ΔH_f° of $\text{HgCl}_2(\text{aq})$, which now leads us to calculate $\Delta H_f^\circ = -55.4 \text{ kcal mol}^{-1}$ and thence $\Delta G_f^\circ = -44.5 \text{ kcal mol}^{-1}$ for $\text{HgCl}_2(\text{c})$.

The best we can do now is to adopt averages of the values quoted above: $\Delta H_f^\circ = -54.0$ and $\Delta G_f^\circ = -43.1 \text{ kcal mol}^{-1}$ for $\text{HgCl}_2(\text{c})$.

There have been several investigations¹²⁶⁻¹²⁸ of the thermodynamics of HgCl_2 in various aqueous alcohol solvent systems. Eliezer and Adida¹²⁹ have measured solubilities of $\text{HgCl}_2(\text{c})$ and $\text{HgBr}_2(\text{c})$ in several organic solvent systems at several temperatures.

Yosim and Mayer¹³⁰ have investigated the Hg-HgCl_2 phase diagram and present evidence that mercury dissolves in molten mercuric chloride with reaction to form mercurous chloride. They have calculated $\Delta H \approx 11 \text{ kcal mol}^{-1}$ for fusion of $\text{Hg}_2\text{Cl}_2(\text{c})$.

Our tabulated ΔH_f° and ΔG_f° for $\text{HgCl}_2(\text{g})$ are consistent with our selections for $\text{HgCl}_2(\text{c})$ and the thermodynamics of vaporization previously cited.^{124,125}

The NBS 270-4 ΔG_f° of $\text{HgBr}_2(\text{c})$ is in excellent agreement with our tabulated ΔG_f° for $\text{HgBr}_2(\text{aq})$ and the solubility of $\text{HgBr}_2(\text{c})$. The ΔH_f° listed in NBS 270-4 for $\text{HgBr}_2(\text{c})$ is in agreement with old calorimetric results.⁵⁴ We combine these values to obtain our tabulated $S^\circ = 41 \text{ cal K}^{-1} \text{ mol}^{-1}$, which is the same as the value listed in NBS 270-4 for $\text{HgBr}_2(\text{c})$. We also have S° of $\text{HgBr}_2(\text{g})$ calculated from molecular constants.^{76,87} Combination of this S° with ΔS° of vaporization⁷⁶ again leads to $S^\circ = 41 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{HgBr}_2(\text{c})$. We obtain ΔH_f° and ΔG_f° for $\text{HgBr}_2(\text{g})$ from corresponding quantities for $\text{HgBr}_2(\text{c})$ and the thermodynamics of vaporization.⁷⁶

The stable form of $\text{HgNH}_2\text{Br}(\text{c})$ at room temperature is an ordered orthorhombic lattice. There is also an unstable cubic form in which the mercury atoms are believed to be disordered in a way that is equivalent to a random walk disorder. Worswick, Mayers, and Staveley¹³¹ have made calorimetric and emf measurements on both forms with results that can be summarized as follows. The third law entropy of the stable orthorhombic form at 298 K is $31.83 \text{ cal K}^{-1} \text{ mol}^{-1}$, which we list in Table I. Similar treatment of heat capacities of the cubic form leads to $S^\circ = S_0 + 31.07 \text{ cal K}^{-1} \text{ mol}^{-1}$, in which S_0 represents the residual entropy at the absolute zero of temperature. Enthalpy of solution measurements have led to ΔH for transformation of cubic to orthorhombic form, and emf measurements have led to ΔG for the same transformation. Combination of these two results gives ΔS of transformation, which leads with the quoted S° of the orthorhombic form to $S^\circ = 31.11 \text{ cal K}^{-1} \text{ mol}^{-1}$ for the cubic form at 298 K. Comparison of the two entropies above shows that S_0 must be very close to zero for the cubic form. Thus it is inferred that the cubic crystal is ordered at the absolute zero, in spite of the absence of any detected transition as the crystal is cooled. A Monte Carlo calculation has suggested¹³¹ that S_0 should be about $1.6 \text{ cal K}^{-1} \text{ mol}^{-1}$ if the "random walk disorder" persisted to the absolute zero.

The NBS 270-4 ΔH_f° values for both the red and yellow forms of $\text{HgI}_2(\text{c})$ are in agreement with the results of old calorimetric measurements.⁵⁴ For $\text{HgI}_2(\text{g})$ the NBS 270-4 S° is in agreement with values calculated^{76,87} from molecular constants. The thermodynamics of vaporization⁷⁶ lead to S° and ΔG_f° of $\text{HgI}_2(\text{c,red})$ and to ΔH_f° and ΔG_f° of $\text{HgI}_2(\text{g})$ in agreement with the values listed in NBS 270-4. There is only fair agreement between the solubility of $\text{HgI}_2(\text{c})$ and the tabulated ΔG_f° values for $\text{HgI}_2(\text{c})$ and $\text{HgI}_2(\text{aq})$.

Morris and Whitlock¹³² have investigated the distribution of HgI_2 between water and CCl_4 , while Kettrup and Specker¹³³ have investigated HgI_2 in combinations of water with tributyl phosphate, cyclohexanone, and isobutyl methyl ketone.

Properties of various compounds and aqueous complexes that contain mercury, a halogen, and an organic component are discussed in section XII.

VIII. HgS , HgSe , and HgTe

Mercuric sulfide is well known in two forms, red (cinnabar) and black (metacinnabar). Dickson and Tunell¹³⁴ and Kullerud¹³⁵ have found that the equilibrium transition temperatures (at 1 atm) from the red to the black form are 344° and 345°C , respectively. The red form is more dense than the black form and is therefore favored at high pressure. Although the red form is thermodynamically more stable than the black form at "ordinary" temperatures, it is the black form that is usually precipitated from aqueous solution.

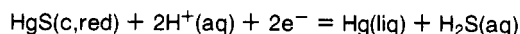
The NBS 270-4 lists $S^\circ = 19.7 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{HgS}(\text{c,red})$, which is the value reported by King and Weller¹³⁶ on the basis of their heat capacity measurements ($52-297 \text{ K}$). We adopt this value.

Taking $\Delta C_p^\circ = 0$ for the red-black transition, we use the NBS 270-4 ΔH_f° and S° values to calculate $T = 786 \text{ K}$ (513°C) for the equilibrium temperature, in poor agreement with the reported^{134,135} value. We shall later choose slightly different ΔH_f° and S° values for $\text{HgS}(\text{c,black})$ and ΔH_f° for $\text{HgS}(\text{c,red})$, partly to improve the agreement between calculated and experimental equilibrium temperatures.

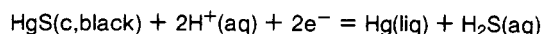
The NBS 270-4 ΔH_f° and ΔG_f° values for $\text{HgS}(\text{c,red})$ are in good agreement with the vapor pressure results of Goldfinger and Jeunehomme.¹³⁷ Further, the thermodynamic properties listed in NBS 270-4 for both $\text{HgS}(\text{c,red})$ and $\text{HgS}(\text{c,black})$ are in reasonable agreement with the high-temperature equilibrium results of Treadwell and Schaufelberger.¹³⁸ On the other hand, more recent vapor pressure measurements by Mitchell and Munir¹³⁹ cast doubt on some of the results of Goldfinger and Jeunehomme¹³⁷ and may be interpreted to indicate that both ΔH_f° and ΔG_f° for $\text{HgS}(\text{c,red})$ are less negative than the NBS 270-4 values. This interpretation is indirectly supported by the electrochemical results of Goates, Cole, and Gray,¹⁴⁰ which lead to ΔG_f° of $\text{HgS}(\text{c,black})$ less negative than the NBS 270-4 value.

There is no single set of thermodynamic properties that is consistent with all of the results cited above, but we suggest that the values we have selected for Table I may be "better" than those listed in NBS 270-4. Our tabulated properties lead to a calculated 330°C for the temperature of equilibrium between red and black forms, in reasonable agreement with the observed transition temperature.

We use our ΔG_f° values with ΔG_f° for $\text{H}_2\text{S}(\text{aq})$ from NBS 270-3 to calculate the following potentials:



$$E^\circ = -0.096 \text{ V}$$



$$E^\circ = -0.085 \text{ V}$$

We use our ΔG_f° of $\text{HgS}(\text{c,black})$ with our ΔG_f° of $\text{Hg}^{2+}(\text{aq})$ and the ΔG_f° for $\text{S}^{2-}(\text{aq})$ from NBS 270-3 to calculate $K_{\text{sp}} = 2 \times 10^{-52}$. It is important to recognize that this calculated K_{sp} is tied to the equilibrium constant for the second ionization of $\text{H}_2\text{S}(\text{aq})$, which in this case means $K = 1 \times 10^{-13}$ that is consistent with NBS 270-3² free energies for $\text{HS}^-(\text{aq})$ and $\text{S}^{2-}(\text{aq})$. This ionization constant and our related K_{sp} are both of the same order as a considerable number of reported^{141,142} values. Although neither the second ionization constant of $\text{H}_2\text{S}(\text{aq})$ nor the K_{sp} of $\text{HgS}(\text{c,black})$ should be regarded as accurately established, there is considerable evidence to support the values above. But it should also be noted that there is now also evidence from Ellis and Giggens-

bach¹⁴³ that the second ionization constant of $\text{H}_2\text{S}(\text{aq})$ is about 10^{-17} or even smaller. If this new second ionization constant is accepted, it follows that the NBS 270-3 ΔG_f° of $\text{S}^{2-}(\text{aq})$ must be changed and that all calculations that involve the concentration or activity of $\text{S}^{2-}(\text{aq})$ in solution must be revised. Because the new¹⁴³ and older^{141,142} ionization constant determinations have been done "reasonably," there is no immediately satisfactory way to resolve this question.

Schwarzenbach and Widmer¹⁴⁴ and more recently Barnes, Romberger, and Stempok¹⁴⁵ have provided excellent reviews of earlier solubility measurements on mercuric sulfide and have reported the results of their own measurements. As a result of all these solubilities, which cover wide ranges of temperature, pH, and solute concentrations, we now have convincing evidence for existence of complex species that have been represented by $\text{HgS}_2^{2-}(\text{aq})$, $\text{Hg}(\text{HS})_2(\text{aq})$, $\text{HgS}(\text{HS})_2^{2-}(\text{aq})$, etc. Because of combined uncertainties in the free energies of $\text{HgS}(\text{c,red})$ and $\text{HgS}(\text{c,black})$ and in the second ionization constant of $\text{H}_2\text{S}(\text{aq})$, we do not write any specific reaction equations with related equilibrium constants or list ΔG_f° values for complex sulfide species in our Table I.

Scott and Barnes¹⁴⁶ have made use of results of solubility studies in planning a method for hydrothermal growth of single crystals of $\text{HgS}(\text{c,red})$.

Ratajczak and Terpilowski¹⁴⁷ have made electrochemical measurements that lead to $\Delta G_f^\circ = -9.1 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta H_f^\circ = -10.8 \pm 0.7 \text{ kcal mol}^{-1}$, and $S^\circ = 22.5 \pm 0.9 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{HgSe}(\text{c})$. Combination of this ΔG_f° with our ΔG_f° for $\text{Hg}^{2+}(\text{aq})$ and the NBS 270-3 ΔG_f° for $\text{Se}^{2-}(\text{aq})$ leads to the solubility product $K_{sp} = 7 \times 10^{-59}$. This value is in good agreement with $K_{sp} = 10^{-59}$ deduced by Lingane and Niedrach¹⁴⁸ from results of their polarographic measurements and ionization constants for $\text{H}_2\text{Se}(\text{aq})$ that were slightly different from those that are consistent with the NBS 270-3 free energies of $\text{H}_2\text{Se}(\text{aq})$, $\text{HSe}^-(\text{aq})$, and $\text{Se}^{2-}(\text{aq})$. More recently, solubility measurements by Mehra and Gubeli¹⁴⁹ have led these workers to report $K_{sp} = 2.5 \times 10^{-57}$ on the basis of ionization constants for $\text{H}_2\text{Se}(\text{aq})$ that are significantly different than those that are consistent with the NBS 270-3² free energies. Combination of their ionization constants with their reported K_{sp} leads us to calculate $\Delta G_f^\circ = -11.9 \text{ kcal mol}^{-1}$ for $\text{HgSe}(\text{c})$. We adopt the thermodynamic properties for $\text{HgSe}(\text{c})$ from Ratajczak and Terpilowski,¹⁴⁷ but note that a free energy from Mehra and Gubeli¹⁴⁹ may be "better" for the mercuric selenide that is precipitated from aqueous solution.

For $\text{HgTe}(\text{c})$ we adopt the thermodynamic properties listed in Table I, based on the electrochemical results of Ratajczak and Terpilowski.¹⁵⁰

There have been a number of investigations of vaporization of $\text{HgSe}(\text{c})$ and $\text{HgTe}(\text{c})$, as described in ref 137, 151–156, and papers cited by these authors. In part because of uncertainties as to concentrations of various species in the gas phase, there are substantial uncertainties in some of the reported results and also disagreements between results of different investigators. But it is encouraging to note that results of several investigators are in reasonable agreement with our tabulated thermodynamic properties of the solid compounds. Because of the various uncertainties, we do not tabulate thermodynamic properties of $\text{HgSe}(\text{g})$ and $\text{HgTe}(\text{g})$.

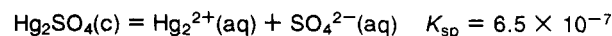
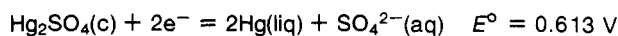
IX. Hg_2SO_4 and HgSO_4

The ΔG_f° values listed in NBS 270-4 for $\text{Hg}_2\text{SO}_4(\text{c})$ and in NBS 270-3 for $\text{SO}_4^{2-}(\text{aq})$ correspond to $E^\circ = 0.6153 \text{ V}$ for the $\text{Hg}_2\text{SO}_4|\text{Hg}$ couple and with our ΔG_f° for $\text{Hg}_2^{2+}(\text{aq})$ to $K_{sp} = 8.0 \times 10^{-7}$ for $\text{Hg}_2\text{SO}_4(\text{c})$. This potential is in good agreement with the emf results of Harned and Hamer,¹⁵⁷ Beck, Dobson, and Wynne-Jones,¹⁵⁸ and Schwabe and Ferse.¹⁵⁹

Further, this K_{sp} agrees well with the value reported by Sharma and Prasad.⁷⁴ There is, however, good evidence in support of slightly smaller potential and K_{sp} values. Covington, Dobson, and Wynne-Jones¹⁶⁰ have carried out very thorough emf measurements and calculations that lead to $E^\circ = 0.6125 \text{ V}$. Other emf measurements by Sharma and Prasad¹⁶¹ have led to $E^\circ = 0.6135 \text{ V}$. The "third law" analysis of Gardner, Mitchell, and Cobble¹⁶² suggests that $E^\circ = 0.6125 \text{ V}$ is the "best" value for the $\text{Hg}_2\text{SO}_4|\text{Hg}$ couple. We also have $K_{sp} = 6.8 \times 10^{-7}$ from the solubility measurements of Brown and Land,¹⁶³ and thence a calculated $E^\circ = 0.6136 \text{ V}$.

As Covington, Dobson, and Wynne-Jones¹⁶⁰ have pointed out, evaluation of the standard potential from measured potentials depends on the ionization constant chosen for $\text{HSO}_4^-(\text{aq})$ and on the ion size parameter used in activity coefficient calculations. Similar considerations have been expressed by Sharma and Prasad^{74,161} in connection with evaluation of both E° and K_{sp} .

On the basis of all of the results described above, we adopt the following potential and solubility product:

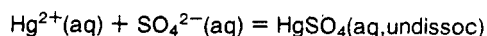


Our $\Delta G_f^\circ = -149.70 \text{ kcal mol}^{-1}$ for $\text{Hg}_2\text{SO}_4(\text{c})$ is consistent with these values.

Heat capacity measurements by Brackett, Hornung, and Hopkins¹⁶⁴ and by Papadopolos and Giauque¹⁶⁵ have led to a reliable $S^\circ_{298} = 47.96 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2\text{SO}_4(\text{c})$, which is the value listed in NBS 270-4. Brackett et al.¹⁶⁴ have discussed the relationship between third law entropies and dE°/dT values for various cells and have concluded that the dE°/dT results are in error. The dE°/dT values from more recently reported work by Beck, Dobson, and Wynne-Jones¹⁵⁸ and Sharma and Prasad¹⁶¹ lead to ΔS° values that are not quite consistent with the entropies. Similarly, there is a difference between the entropies already cited and that calculated from the $d \ln K_{sp}/dT$ results of Sharma and Prasad.⁷⁴ We therefore accept the third law^{164,165} S°_{298} for $\text{Hg}_2\text{SO}_4(\text{c})$ and combine with our ΔG_f° to obtain the ΔH_f° listed in Table I.

The ΔH_f° of $\text{HgSO}_4(\text{c})$ listed in NBS 270-4 is consistent with old calorimetric results⁵⁴ and is adopted for our Table I.

The ΔG_f° values for $\text{HgSO}_4(\text{aq})$ and $\text{Hg}^{2+}(\text{aq})$ in NBS 270-4 and the ΔG_f° for $\text{SO}_4^{2-}(\text{aq})$ in NBS 270-3 lead to $K = 26$ for



The same value has been reported by Posey and Taube¹⁶⁶ for solutions with ionic strength 0.32 M . In the absence of activity coefficients, we accept this K and the related ΔG_f° for $\text{HgSO}_4(\text{aq})$, which differs slightly from that in NBS 270-4 because of the difference in ΔG_f° values for $\text{Hg}^{2+}(\text{aq})$.

X. Cyanides and Thiocyanates of Mercury

The NBS 270-4 and 270-3 ΔG_f° values lead to the equilibrium constants for mercuric cyanide complexes that are summarized in Table IV. These values are in close agreement with those reported by Anderegg.¹⁶⁷ Somewhat smaller K values have been reported by Christensen, Izatt, and Eattough.¹⁶⁸ The second, third, and fourth constants are in reasonable agreement with polarographic results ($\mu = 2.0 \text{ M}$ and 30°C) of Newman, Cabral, and Hume.¹⁶⁹

There have been several claims¹⁷⁰ concerning complex ions such as $\text{Hg}(\text{CN})_n^{2-n}(\text{aq})$ with $n > 4$, but it now appears certain from the spectroscopic work of Ashurst, Finkelstein, and Gould¹⁷¹ that these earlier reports are mistaken.

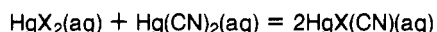
The ΔH_f° values listed in NBS 270-4 for $\text{Hg}(\text{CN})^+(\text{aq})$,

TABLE IV. Equilibrium Constants at 298 K for Mercuric Cyanide and Thiocyanate Complexes

Reaction	<i>K</i>	
	CN ⁻	SCN ⁻
Hg ²⁺ (aq) + L ⁻ (aq) = HgL ⁺ (aq)	2.0 × 10 ¹⁷	1 × 10 ⁹
HgL ⁺ (aq) + L ⁻ (aq) = HgL ₂ (aq)	1.7 × 10 ¹⁷	1 × 10 ⁸
HgL ₂ (aq) + L ⁻ (aq) = HgL ₃ ⁻ (aq)	5.5 × 10 ³	7 × 10 ²
HgL ₃ ⁻ (aq) + L ⁻ (aq) = HgL ₄ ²⁻ (aq)	1.0 × 10 ³	7 × 10 ¹
Hg ²⁺ (aq) + 4L ⁻ (aq) = HgL ₄ ²⁻ (aq)	1.9 × 10 ⁴¹	5 × 10 ²¹

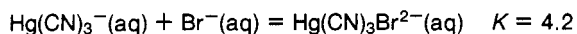
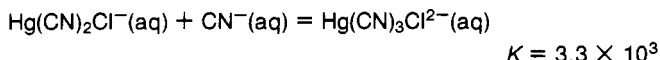
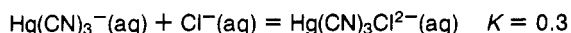
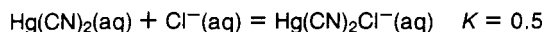
Hg(CN)₂(aq), and Hg(CN)₃⁻(aq) are in reasonable agreement with results of calorimetric investigations.^{168,172,173} But the reported^{168,172,173} ΔH° values for formation of Hg(CN)₄²⁻(aq) from Hg(CN)₃⁻(aq) and from Hg²⁺(aq) range from 0.3 to 4.3 kcal mol⁻¹ more exothermic than those calculated from the NBS 270-4 ΔH° values. Our adopted ΔH° values are based on those tabulated in NBS 270-4 for Hg(CN)_{*n*}²⁻ⁿ(aq) (*n* = 1, 2, 3) after adjustment for our new ΔH° of Hg²⁺(aq), while our ΔH° for Hg(CN)₄²⁻(aq) is intended to adhere more closely to calorimetric results cited above. Entropies have been calculated from our (Table I) free energies and enthalpies, as those listed in NBS 270-4 are inconsistent with the other tabulated properties.

Beck and Gaizer¹⁷⁴ have investigated equilibria of type



and have reported $K = 8.46$ for $X = \text{Cl}^-$, $K = 1.94$ for $X = \text{Br}^-$, and $K = 0.11$ for $X = \text{I}^-$. More recently, Coleman et al.¹⁷⁵ have reported $K = 0.14$ for the reaction with $X = \text{I}^-$. We use these results in calculating our tabulated ΔG° values for HgCl(CN)(aq), HgBr(CN)(aq), and HgI(CN)(aq).

Free energies from NBS 270-4 and 270-3 lead to the following equilibrium constants:



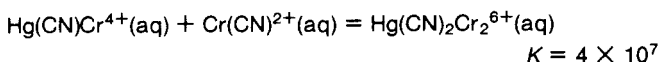
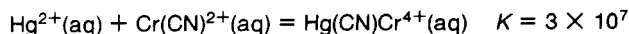
These values are in reasonable agreement with the equilibrium constants reported by Newman and Hume¹⁷⁶ and by Agrawal, Vishnu, and Mehrotra¹⁷⁷ for 2.0 and 4.0 *M* solutions.

For association of thiourea (tu) with mercuric cyanide, we have the following from the calculations of Eatough, Izatt, and Christensen:¹⁷⁸



These values and related ΔH° values¹⁷⁸ are presumably to be preferred to $K = 93$ and $K = 355$ reported previously^{179,180} for these same reactions. There are also equilibrium constants and enthalpies for these reactions in various water-ethanol¹⁸⁰ and water-formamide¹⁷⁹ systems, with the latter investigation including results for 100% formamide.

Following the initial observation by Birk and Espenson¹⁸¹ of the "unexpected" stability of a species formed by association of Hg²⁺(aq) with Cr(CN)₂²⁺(aq), there have been several investigations of this and related reactions. For example, from Frank and Anson¹⁸² we have the following:



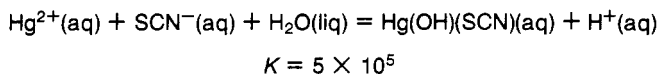
We also have equilibrium constants for interaction of Hg(CN)₂(aq) with Fe(CN)₆⁴⁻(aq), Mo(CN)₈³⁻(aq), and Ru(CN)₆⁴⁻(aq) from the work of Beck and Porzsoit.¹⁸³

Cell measurements by Rock¹⁸⁴ have led to a reported $K_{\text{sp}} = 1.9 \times 10^{-37}$ for mercurous cobalticyanide, (Hg₂)₃[Co(CN)₆]₂(c). This reported K_{sp} was based in part on $E^\circ = 0.789$ V (rather than $E^\circ = 0.796$ V cited in our section V) for the Hg₂²⁺|Hg potential. Recalculation of the reported¹⁸⁴ results with this latter potential now leads to a new $K_{\text{sp}} = 3.7 \times 10^{-38}$. Rock¹⁸⁴ has pointed out that the solid phase referred to as (Hg₂)₃[Co(CN)₆]₂(c) is probably the tetrahydrate. Similar considerations with respect to calculations and solid phase compositions apply to several other reported solubility products.^{141,142}

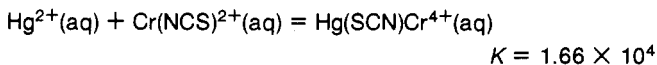
We have $K_{\text{sp}} = 1.1 \times 10^{-12}$ for (Hg₂)₂[Fe(CN)₆](c) and $K_{\text{sp}} = 8.5 \times 10^{-21}$ for (Hg₂)₃[Fe(CN)₆]₂(c), as quoted by Sillen.¹⁴¹ Sillen¹⁴¹ has also cited $K_{\text{sp}} = 5 \times 10^{-40}$ for Hg₂(CN)₂(c), from which we calculate our tabulated ΔG° for mercurous cyanide.

We adopt equilibrium constants for formation of mercuric thiocyanate complexes as listed in Table IV. These values are based on results reported by Tanaka, Ebata, and Morayama¹⁸⁵ and more recently by Ciavatta and Grimaldi.¹⁸⁶ Our ΔG° values for these species differ only slightly from those previously listed in NBS 270-4, which were apparently based largely on the results of Tanaka et al.¹⁸⁵ Our ΔH° values are based on the calorimetric results of Ahrlund and Kullberg.¹⁸⁷ These values are in reasonable agreement with earlier results, which have been reviewed by Ahrlund and Kullberg.¹⁸⁷

Ciavatta, Grimaldi, and Mangone⁶⁵ have interpreted their results of investigations of hydrolysis of mercuric thiocyanate solutions in terms of the following:



Falk and Linck¹⁸⁸ have reported equilibrium constants for reaction between Hg²⁺(aq) and Co(SCN)₂²⁺(aq). Armor and Haim¹⁸⁹ have reported equilibrium constants at several temperatures (and derived ΔH° and ΔS° values) for the reaction



Sillen¹⁴¹ has listed solubility products for Hg₂(SCN)₂(c) from which we select $K_{\text{sp}} = 2 \times 10^{-20}$ and calculate the ΔG° that is listed in Table I. Sillen¹⁴¹ has also listed solubility products for compounds of type M[Hg(SCN)₄] in which M represents Co²⁺, Cu²⁺, Zn²⁺, and Cd²⁺. Because of disagreements between the results of different investigators and uncertainties about the state of hydration of the solid phases, we do not tabulate ΔG° values for any of these compounds.

Czakis-Sulikowska¹⁹⁰ has reported stability constants for mixed complexes involving SCN⁻ with NO₂⁻, Cl⁻, Br⁻, and I⁻. Some related equilibrium constants have also been reported by Yakhkind and Gyunter.¹⁹¹ In an earlier paper these latter workers report¹⁹² equilibrium constants for formation of Hg₂(SCN)₂²⁺(aq) and also for Hg₂Br₂²⁺(aq) in solutions with high ionic strength.

XI. Other Inorganic Complexes and Compounds

For the hydride HgH(g) we adopt $S^\circ = 52.50$ cal K⁻¹ mol⁻¹ and $\Delta H^\circ_f = 57$ kcal mol⁻¹ from spectroscopic data as discussed by Feber and Herrick¹⁹³ and also in the JANAF tables.⁷⁶ These values and the derived ΔG°_f are close to those listed in NBS 270-4.

Free energies from NBS 270-4 and 270-3 lead to the following solubility products:

TABLE V. Equilibrium Constants at 298 K for Formation of Amine Complexes

Reaction	K			
	NH ₃	CH ₃ NH ₂	n-C ₄ H ₉ NH ₂	en
Hg ²⁺ (aq) + L(aq) = HgL ²⁺ (aq)	6.3 × 10 ⁸	4.6 × 10 ⁸	5.5 × 10 ⁸	2 × 10 ¹⁴
HgL ²⁺ (aq) + L(aq) = HgL ₂ ²⁺ (aq)	5.0 × 10 ⁸	1.6 × 10 ⁹	2.5 × 10 ⁹	1 × 10 ⁹
HgL ₂ ²⁺ (aq) + L(aq) = HgL ₃ ²⁺ (aq)	10	(2)	8	
HgL ₃ ²⁺ (aq) + L(aq) = HgL ₄ ²⁺ (aq)	6	(2)	10	
Hg ²⁺ (aq) + 4L(aq) = HgL ₄ ²⁺ (aq)	2.0 × 10 ¹⁹	3 × 10 ¹⁸	1 × 10 ²⁰	



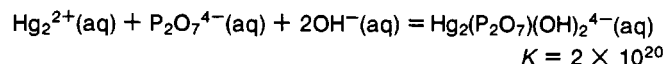
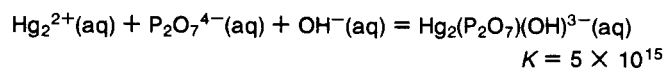
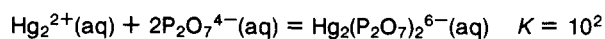
These K_{sp} values for mercuric and mercurous selenites are both in agreement with values cited by Sillen.¹⁴¹

We are unable to interpret the thermal data reported by Pron' and Markovskii¹⁹⁴ for mercuric tellurite, HgTeO₃, and therefore do not list this compound in Table I.

For the aqueous ammonia complexes of mercuric ion we adopt the equilibrium constants listed in Table V, taken from the recent report of Bjerrum.¹⁹⁵ The product of the first two constants is in excellent agreement with the corresponding results of Wirth and Davidson.¹⁹⁶ Our ΔG_f° values in Table I for these complexes are not much different from those listed earlier in NBS 270-4. The ΔH_f° values for the Hg(NH₃)_n²⁺(aq) complexes in NBS 270-4 are in good agreement with the calorimetric results of Yatsimirskii and Milyukov.¹⁹⁷ Earlier calorimetric results from Fyfe¹⁹⁸ do not permit calculation of ΔH values for well specified reactions.

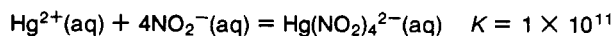
Although addition of complexing agents to mercurous compounds or their aqueous solutions often results in disproportionation to elemental mercury and a soluble complex or a precipitate containing Hg(II), there are some complexes of Hg₂²⁺(aq) that are stable enough to exist at reasonable concentrations in solution. Some examples are various phosphate complexes that we now consider.

Yamane and Davidson¹⁹⁹ and Watters and Simonaitis²⁰⁰ have reported a considerable number of stability constants as summarized below (some are average values):



Various other equilibrium constants for complexes of Hg₂²⁺(aq) with P₃O₁₀⁵⁻(aq) and P₄O₁₃⁶⁻ have also been reported.^{199,200} We list ΔG_f° values for the pyrophosphate complexes, but are unable to do the same for the other species because we have no ΔG_f° values for the aqueous polyphosphate ions.

From the work of Tumavouri²⁰¹ we take

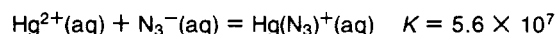


and calculate the corresponding ΔG_f° of Hg(NO₂)₄²⁻(aq).

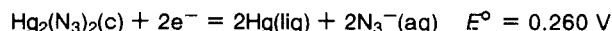
Davis and Irish²⁰² have reviewed work on the association of Hg²⁺(aq) with NO₃⁻(aq) and have carried out thorough Raman spectral investigations of aqueous mercuric nitrate solutions with results that are consistent with $K_1 = 1.3$ and $K_2 = 1.0$ for stepwise formation of HgNO₃⁺(aq) and Hg(NO₃)₂(aq). More recent Raman work²⁰³ suggests a slightly larger K_1 and smaller K_2 , consistent with our tabulated ΔG_f° values.

For mercuric azide complexes we have the following equilibrium constants (28°C) from the work of Musgrave and Keller:²⁰⁴

librium constants (28°C) from the work of Musgrave and Keller:²⁰⁴

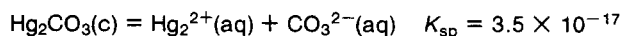
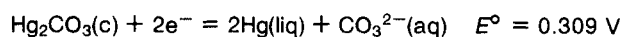


Sillen¹⁴¹ has listed $K_{\text{sp}} = 7.1 \times 10^{-10}$, based on the work of Suzuki,²⁰⁵ as the solubility product for mercurous azide, Hg₂(N₃)₂(c). This value is in good agreement with $K_{\text{sp}} = 7.0 \times 10^{-10}$ listed in the *Chemical Abstracts*²⁰⁵ summary of Suzuki's work, which is described in terms of HgN₃. On the other hand, the free energies listed in NBS 270-4 and 270-3 lead to $K_{\text{sp}} = 7.8 \times 10^{-19}$. Further, Gray and Waddington²⁰⁶ have combined their properties for N₃⁻(aq) with Suzuki's results to obtain a ΔG_f° that is in turn consistent with the solubility product we have calculated from NBS free energies. Because it seems likely that Gray and Waddington²⁰⁶ and the compilers of NBS 270-4 have "correctly" interpreted Suzuki's results in terms of Hg₂(N₃)₂(c) and Hg₂²⁺(aq), we adopt $K_{\text{sp}} = 7.8 \times 10^{-19}$ for mercurous azide, along with the corresponding ΔG_f° . We also adopt the following potential:

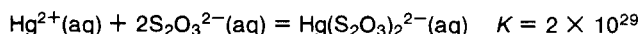


Calorimetric measurements by Gray and Waddington²⁰⁶ have led to $\Delta H^\circ = -29.87 \text{ kcal mol}^{-1}$ for precipitation of Hg₂(N₃)₂(c), in reasonable agreement with their interpretation of the temperature coefficient results of Suzuki.²⁰⁵ We use this calorimetric ΔH° to calculate the ΔH_f° and combine with the ΔG_f° to obtain the S° of Hg₂(N₃)₂(c).

The thermodynamic properties listed in NBS 270-4 for mercurous carbonate are consistent with the emf results of Sae-gusa²⁰⁷ and also the following potential and solubility product:

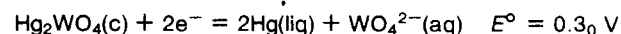
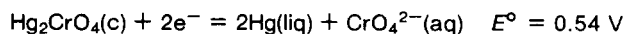


Polarographic measurements by Nyman and Salazar²⁰⁸ have led to the following equilibrium constants:



The above K values are in good agreement with values from Toropova as quoted by Sillen.¹⁴¹

Sillen¹⁴¹ has listed two values for log K_{sp} (-17.89 and -13.71) for mercurous iodate. We are unable to choose between these values and therefore do not calculate a free energy for Hg₂(IO₃)₂(c). Sillen¹⁴¹ has also listed log $K_{\text{sp}} = -8.70$ for mercurous chromate and log $K_{\text{sp}} = -16.96$ (18°C) for mercurous tungstate. We combine these values with the Hg₂²⁺|Hg potential to calculate the following potentials:



Using the free energy of CrO₄²⁻(aq) from NBS 270-4, we also calculate the ΔG_f° of Hg₂CrO₄(c) as in Table I.

Sillen¹⁴¹ has quoted (from Toropova) the following:



Values of ΔH° and ΔS° are based on stability constants from 15 to 30°C. Note that $\text{Hg}(\text{SeCN})_4^{2-}(\text{aq})$ appears to be considerably less stable than $\text{Hg}(\text{CN})_4^{2-}(\text{aq})$ and considerably more stable than $\text{Hg}(\text{SCN})_4^{2-}(\text{aq})$.

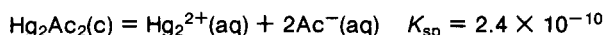
Bernard and Busnot²⁰⁹ have reported $\Delta H_f^\circ = 66 \text{ kcal mol}^{-1}$ for mercuric cyanamide, $\text{HgCN}_2(\text{c})$, on the basis of their calorimetric measurements.

The NBS 270-4 lists ΔH_f° values for a considerable number of inorganic compounds of mercury, such as $\text{HgX}_2 \cdot n\text{NH}_3(\text{c})$, etc. Because the original experimental results for these compounds have been cited^{54,210} and discussed⁵⁴ earlier, we omit these compounds from our discussion and also from our Table I.

XII. Compounds and Complexes Containing Organic Components

Cox and Pilcher¹⁰ have provided an excellent review of the thermochemical properties of a number of organomercury compounds. The ΔH_f° values listed by Cox and Pilcher¹⁰ are in generally satisfactory agreement with those listed in NBS 270-4. Here we also call attention to the recent calorimetric investigation of mercury diphenyl by Carson and Wilmshurst²¹¹ and to the investigation of redistribution equilibria of organomercury compounds by Reynolds and Daniel.²¹²

Combination of ΔG_f° values for mercurous acetate and aqueous acetate ion as listed in NBS 270-4 and NBS 270-3 leads to $E^\circ = 0.5047 \text{ V}$ for the $\text{Hg}_2(\text{Ac})_2|\text{Hg}$ couple. Although Gryzin²¹³ has reported $E^\circ = 0.4982 \text{ V}$ for this couple, a value more positive than 0.5047 V seems better. Larson²¹⁴ has reported $E^\circ = 0.5116 \text{ V}$, but Covington, Talukdar, and Thirsk²¹⁵ have recalculated to obtain $E^\circ = 0.5109$ and 0.5111 V, and have also reported $E^\circ = 0.5113 \text{ V}$ based on their own measurements. Most recently, Chen and Pan²¹⁶ have found $E^\circ = 0.5117 \text{ V}$. We therefore adopt the following:

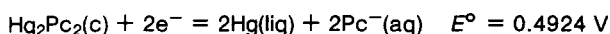


The dE°/dT results of Chen and Pan²¹⁶ lead to $S^\circ = 71 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $\Delta H_f^\circ = -201.4 \text{ kcal mol}^{-1}$ for $\text{Hg}_2\text{Ac}_2(\text{c})$. Similar results from Larson²¹⁴ (his reported calculations are mistaken) and Gryzin²¹³ lead to larger entropies and less exothermic ΔH_f° values. On the basis of these values and old calorimetric results (difficult to interpret) cited by Bichowsky and Rossini,⁵⁴ we adopt $S^\circ \approx 74 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $\Delta H_f^\circ = -201 \text{ kcal mol}^{-1}$ for $\text{Hg}_2\text{Ac}_2(\text{c})$. A third law entropy would be useful.

Basu and Aditya²¹⁷ have investigated the $\text{Hg}_2\text{Ac}_2|\text{Hg}$ electrode in various water-dioxane mixtures from 15 to 35°C.

The NBS 270-4 and 270-3 free energies lead to $K = 1.2 \times 10^3$ for formation of $\text{HgAc}^-(\text{aq})$ from the ions. Martell¹⁴¹ has listed $\beta_2 = 2.7 \times 10^8$ for formation of $\text{HgAc}_2(\text{aq})$ at an unspecified temperature, based on a paper we have not read. We also have $\beta_1 = 3.6 \times 10^5$, $\beta_2 = 2.0 \times 10^9$, $\beta_3 = 1.9 \times 10^{13}$, and $\beta_4 = 1.2 \times 10^{11}$ from Banerjee and Singh.²¹⁸ The most recent result is $\beta_1 = 6.9 \times 10^5$ from Lisovaya et al.²¹⁹ Because we are unable to reconcile all these values, we omit mercuric acetate species from our Table I.

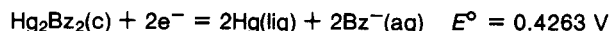
Covington and Srinivasan²²⁰ have made measurements with sodium-responsive glass electrodes in cells without liquid junction and obtained the following standard potential for mercurous picrate:



Combination of this potential with that for the $\text{Hg}_2^{2+}|\text{Hg}$ couple leads to $K_{\text{sp}} = 5.4 \times 10^{-11}$ for mercurous picrate, $\text{Hg}_2\text{Pc}_2(\text{c})$. This value is in good agreement with $K_{\text{sp}} = 4.9 \times 10^{-11}$ from solubility measurements.²²⁰ The emf method

used by Covington and Srinivasan²²⁰ should have useful applications to other systems.

Bertram and Bone²²¹ have measured the mercurous benzoate potential from 25 to 40°C and have reported for 25°C the following:



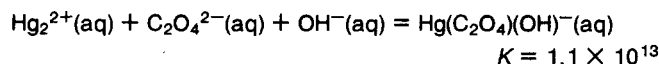
This potential corresponds to $K_{\text{sp}} = 3.2 \times 10^{-13}$ for $\text{Hg}_2\text{Bz}_2(\text{c})$. The ΔH° and ΔS° values reported by Bertram and Bone²²¹ have been calculated incorrectly; correct values are $\Delta H^\circ = -29.3 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = -32.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ for the cell reaction. Again, a third law entropy would be useful.

Free energies from NBS 270-4 and 270-3 for mercurous oxalate and oxalate ion lead to $E^\circ = 0.418$ for the $\text{Hg}_2\text{C}_2\text{O}_4|\text{Hg}$ couple and to $K_{\text{sp}} = 1.7 \times 10^{-13}$ for $\text{Hg}_2\text{C}_2\text{O}_4(\text{c})$. This value is in good agreement with the value quoted by Latimer,²²² based on Brodsky's calculations with results of earlier measurements.

The ΔG_f° listed in NBS 270-4 for $\text{Hg}(\text{C}_2\text{O}_4)_2^{2-}$ should (we believe) refer to the mercurous complex, $\text{Hg}_2(\text{C}_2\text{O}_4)_2^{2-}(\text{aq})$. Using the NBS 270-4 value for this free energy with that for aqueous oxalate ion, we calculate the following:

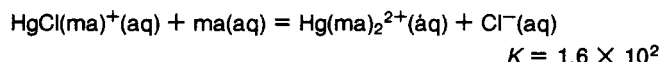
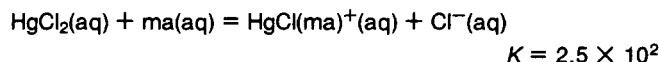


NBS free energies also lead to another equilibrium constant:



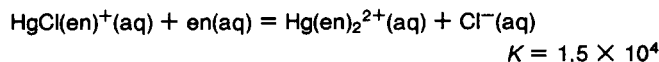
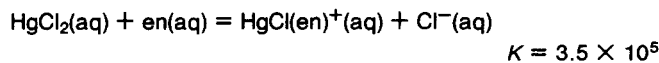
Both of these equilibrium constants are consistent with the results of Yamane and Davidson.¹⁹⁹

Equilibrium constants for formation of $\text{Hg}(\text{II})$ -methylamine complexes, based on the work of Bjerrum,¹⁹⁵ are summarized in Table V. We also have the following equilibrium constants (ma = methylamine) from Partridge, Christensen, and Izatt:²²³



The ΔG_f° values listed in Table I are consistent with the equilibrium constants above and those in Table II. Our adopted ΔH_f° and S° values are based on the calorimetric results of Partridge, Christensen, and Izatt.²²³

"Best" formation constants for $\text{Hg}(\text{II})$ -ethylenediamine complexes, based on the investigations of Watters and Mason²²⁴ and of Roe, Masson, and Nyman,²²⁵ are listed in Table V. We also have the following equilibrium constants (en = ethylenediamine) from the work of Partridge, Christensen, and Izatt:²²³



Combination of these latter values with formation constants for $\text{HgCl}^+(\text{aq})$ and $\text{HgCl}_2(\text{aq})$ from Table II leads to $K = 0.8 \times 10^{23}$ for



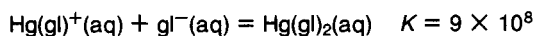
This calculated value is in remarkably good agreement with the corresponding $K = 2 \times 10^{23}$ from formation constants^{224,225} in Table V.

Roe, Masson, and Nyman²²⁵ have calculated $\Delta H^\circ =$

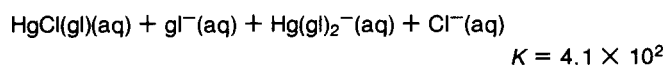
$-32.9 \text{ kcal mol}^{-1}$ (from $d \ln K/dT$) for the reaction represented by eq 14. Partridge, Christensen, and Izatt²²³ have made calorimetric measurements leading to $\Delta H^\circ = -17.7 \text{ kcal mol}^{-1}$ for replacement of both Cl^- in $\text{HgCl}_2(\text{aq})$ to yield $\text{Hg}(\text{en})_2^{2+}(\text{aq})$, which we combine with ΔH_f° values already cited to obtain $\Delta H^\circ = -30.4 \text{ kcal mol}^{-1}$ for reaction 14. The $2.5 \text{ kcal mol}^{-1}$ difference between these two ΔH° values is not unreasonably large in view of the difference in paths and the uncertainty in ΔH_f° of $\text{HgCl}_2(\text{aq})$ that has been discussed previously. We have weighted the calorimetric results most heavily in obtaining our tabulated ΔH_f° values.

Watters and Mason²²⁴ have also reported equilibrium constants for such species as $\text{Hg}(\text{en})(\text{OH})^+(\text{aq})$, $\text{Hg}(\text{en})_2\text{H}^{3+}(\text{aq})$, etc.

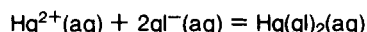
The free energies in NBS 270-4 and 270-3 for mercuric glycinate (gl^-) complexes and glycinate ion lead to the following:



These values are in good agreement with results cited by Martell.¹⁴¹ We also have the following equilibrium constants from the work of Partridge, Christensen, and Izatt:²²³



Combination of these values with formation constants from Table II leads to $K = 1.5 \times 10^{19}$ for



compared to 1.8×10^{19} from the product of the stepwise constants given above. The ΔH_f° values listed in NBS 270-4 for $\text{HgCl}(\text{gl})(\text{aq})$ and $\text{Hg}(\text{gl})_2(\text{aq})$ are in good agreement with the calorimetric results of Partridge, Christensen, and Izatt.²²³

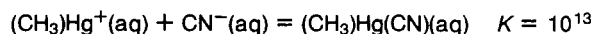
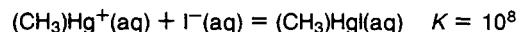
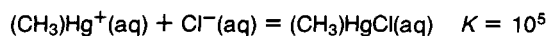
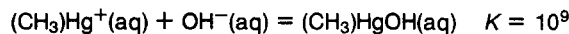
Results of many investigations^{141,142,226-229} are in reasonable agreement with $\log K = 22$ for the formation of the aqueous $\text{Hg}(\text{II})$ -EDTA complex, but some of these investigations illustrate a common problem in coordination chemistry, as follows. Calorimetric measurements by three sets of investigators²²⁶⁻²²⁸ have led to $\Delta H = -18.9$, -19.2 , and $-18.9 \text{ kcal mol}^{-1}$ for complex formation, while application of $d \ln K/dT$ to K values at different temperatures has led Moeller and Chu²²⁹ to $\Delta H^\circ = -9.3 \text{ kcal mol}^{-1}$ for this same reaction. This discrepancy of $\sim 10 \text{ kcal mol}^{-1}$, which is probably due to error in the latter work,²²⁹ corresponds to a discrepancy of $\sim 30 \text{ cal K}^{-1} \text{ mol}^{-1}$ in the entropy and is more than enough to invalidate molecular interpretations.

Carson, Laye, and Steele²³⁰ have carried out calorimetric investigations of complexing of $\text{Hg}^{2+}(\text{aq})$ by *trans*-1,2-diaminocyclohexanetetraacetic acid (CDTA) and have compared their $\Delta H = -16.05 \text{ kcal mol}^{-1}$ with -16.60 and $-18.9 \text{ kcal mol}^{-1}$ from earlier calorimetric investigations. We also note that two applications²³¹ of $d \ln K/dT$ have led to $\Delta H^\circ = -14.1$ and $-13.7 \text{ kcal mol}^{-1}$ for this complexing reaction.

Martell^{141,142} has listed many stability constants (and some enthalpies) for organic complexes of mercury. Ashcroft and Mortimer²³² have compiled a useful collection of information (emphasis on thermochemical properties) about such complexes. Here we call attention to only two additional investigations. Goddard, Lodam, Ajayi, and Campbell²³³ have made electrochemical and calorimetric measurements on complexes of $\text{Hg}^{2+}(\text{aq})$ with urea, semicarbazide, and sulfur and selenium analogs of these compounds. Ashurst, Finkelstein, and Rice²³⁴ have carried out extensive investigations of cyanide-xanthate mixed complexes of $\text{Hg}^{2+}(\text{aq})$ and have re-

ported equilibrium constants over the range 5 – 50°C with related thermodynamic quantities for complex formation.

We have a considerable number of equilibrium constants for association of $(\text{CH}_3)_2\text{Hg}^+(\text{aq})$ with various ligands.²³⁵ Some representative values follow:



Equilibrium constants for similar reactions with other ligands and also for reactions of various ligands with $(\text{CH}_3\text{CH}_2)_2\text{Hg}^+(\text{aq})$ have been reported²³⁵ along with solubility products for PhHgX and $(\text{CH}_3)_2\text{HgX}$ (Ph = phenyl and X = halide). Enthalpy and entropy changes are available for some of these reactions. We also have ionization constants²³⁶ for fluoroalkylmercuric hydroxide and halides.

Smith and Bertrand²³⁷ have measured solubilities of dimethylmercury in water and various salt solutions.

Mansy, Wood, Sprowles, and Tobias²³⁸ have recently reported results of their investigation (by Raman spectroscopy) of binding of $(\text{CH}_3)_2\text{Hg}^+$ to pyrimidine nucleosides and nucleotides, and have also provided numerous references to related work involving mercury and/or important biomolecules.

Barnes²³⁹ has reported enthalpies of decomposition of mercuric halide-dioxane complexes and has discussed the results in relation to structures of these compounds.

Farhangi and Graddon²⁴⁰ have reported thermodynamic data for reactions of HgX_2 compounds with various Lewis bases in benzene solution.

Brusset and Madaule-Aubry²⁴¹ have reported thermodynamic data for $\text{HgCl}_2 \cdot 2\text{CH}_3\text{OH}(\text{c})$. We do not know the source of the properties for $\text{HgCl}_2 \cdot \text{CH}_3\text{OH}(\text{c})$ that are listed in NBS 270-4.

XIII. Appendix

In this Appendix we call attention to a few investigations that were not cited in the main body of our review.

Carlson et al.²⁴² have measured the vapor pressure of $\text{Hg}(\text{liq})$ at several temperatures, with results leading to a ΔH_f° for $\text{Hg}(\text{liq})$ at 298 K in good agreement with our tabulated value. This paper is noteworthy for its analysis of the Knudsen method for vapor pressure measurements.

Onat²⁴³ has reported solubilities of $\text{Hg}(\text{liq})$ in water from 25 to 80°C . The results do not resolve the uncertainties in thermodynamic properties of $\text{Hg}(\text{aq})$ that were discussed in section III.

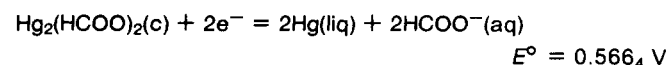
Case and Bignold²⁴⁴ and Johansson et al.²⁴⁵ have investigated the $\text{HgO}|\text{Hg}$ electrode over wide ranges of temperature and found that it is a useful reference electrode for alkaline solutions at high temperatures.

Ammlung and Brill²⁴⁶ have investigated " HgBr " in the solid state and found that it is a homogeneous equilibrium mixture of HgBr_2 , HgBr , and HgI_2 .

Distribution measurements by Nikolic and Gal²⁴⁷ have led to K values (55 – 85°C) for mercuric chloride and bromide complexes in the melt of $\text{NH}_4\text{NO}_3 \cdot 2\text{H}_2\text{O}$.

Munir et al.²⁴⁸ have investigated the sublimation of $\text{HgS}(\text{c,black})$ with results suggesting that the ΔH_f° is less negative than the values we ($-12.0 \text{ kcal mol}^{-1}$) and NBS 270-4 ($-12.8 \text{ kcal mol}^{-1}$) have listed for this substance.

Ostannii et al.²⁴⁹ have made cell measurements on mercurous formate electrodes that lead to the following at 298 K :



This potential corresponds to $\Delta G^\circ = -141.7 \text{ kcal mol}^{-1}$ for $\text{Hg}_2(\text{HCOO})_2(\text{c})$. Their dE°/dT ($10\text{--}30^\circ\text{C}$) leads to $\Delta H^\circ = -180 \text{ kcal mol}^{-1}$ and $S^\circ = 41 \text{ cal K}^{-1} \text{ mol}^{-1}$ for $\text{Hg}_2(\text{HCOO})_2(\text{c})$.

Sundberg and Martin²⁵⁰ provide an extensive review of interactions of mercury (and other metal ions) with histidine and related imidazole derivatives in connection with biochemical problems.

Puhl and Henneke²⁵¹ have investigated the interaction of pyridine and 2,2'-bipyridyl and bis(pentafluorophenyl)mercury in CCl_4 and C_6H_6 . They have carried out a thorough analysis of their calorimetric and nmr results in relation to derived K and ΔH° values.

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