Mercury: Thermodynamic Properties, Chemical Equilibria, and Standard Potentials

LOREN G. HEPLER* and GERD OLOFSSON[1]

Department of Chemistry, University of Lethbridge, Lethbridge, Alberta, Canada

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Contents

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 $\Delta H_f°$ of Cl^-(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 $\Delta G°$, $\Delta H°$, and $\Delta S°$ 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 publications[21-24] 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 Wilkinson[25] 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 HgO(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}
Hg(liq)	*0*	*0*	*18.17*[30,31]
Hg(g)	*14.655*	*7.613*	*41.79*
Hg(aq)	3.33[43]	8.9[43]	−0.5
Hg^+(g)	*256.82*		
Hg^{2+}(g)	*690.83*		
Hg^{2+}(aq)	40.67[53]	39.365[56]	-8.6_6[56]
Hg^{3+}(g)	*1480.*		
Hg_2(g)	*26.0*	*16.3*	*68.82*
Hg_2^{2+}(aq)	39.87[56]	36.713[56]	15.7_2[56]
HgO(c, red, orthorh)	*−21.71*	*−13.995*	*16.80*[51]
HgO(c, yellow, orthorh)	−21.71[53]	−13.970[53]	16.70[53]
HgO(c, red, hexag)	−21.59[53]	−13.940[53]	17.0_3[53]
HgO(g)			*57.8*[87]
HgH(g)	57[76,193]	51	52.50[76,193]
$Hg(OH)^+$(aq)	−20.2	-12.4_3[b]	16.5
$Hg(OH)_2$(aq, undiss)	−86.0	−65.6[b]	30.2
$Hg(OH)_3^-$(aq)		−102.1[c]	
$HHgO_2^-$(aq)		−45.4[b]	
HgF(g)	~0.7[76]	~−4.4[76]	59.34[76]
HgF^+(aq)	−38.0[b]	−29.4[b]	−2[b]
Hg_2F_2(c)	−116	−103[77]	(40)
HgCl(g)	20	15	62.1
$HgCl^+$(aq)	−4.7[b]	−1.2[b]	17[b]
$HgCl_2$(c)	−54.0	−43.1	*34.9*
$HgCl_2$(g)	−34.2[124]	−33.9[124]	70.43[76,124]
$HgCl_2$(aq, undiss)	−51.9[b]	−41.3[b]	36[b]
$HgCl_3^-$(aq)	−93.1[b]	−73.8[b]	49[b]
$HgCl_4^{2-}$(aq)	−132.6[b]	−106.7[b]	69[b]
HgCl(OH)(aq, undiss)	−69.0[118]	−53.1[118,119]	32
Hg_2Cl_2(c)	-63.47_5[56,86]	−50.376[56,86]	45.7_5[56,86]
HgBr(g)	~25[76]	~16[76]	64.9[76]
$HgBr^+$(aq)	1.3[b]	2.2[b]	18[b]
$HgBr_2$(c)	*−40.8*	*−36.6*	*41.*
$HgBr_2$(g)	−20.7[76]	−27.2[76]	76.511[76]
$HgBr_2$(aq, undiss)	−38.6[b]	−34.1[b]	40[b]
$HgBr_3^-$ (aq)	−70.3[b]	−61.9[b]	61[b]
$HgBr_4^{2-}$(aq)	−103.2[b]	−88.6[b]	73[b]
HgBr(OH)(aq, undiss)		−49.7[120]	
HgBrCl(g)			*71.55*
HgBrCl(aq, undiss)		−38.6[b]	
Hg_2Br_2(c)	−49.46	−43.280[92,93]	52.0
HgI(g)	31.6[99]	21.9[99]	*67.26*
HgI^+(aq)	10.1[b]	9.6[b]	18[b]
HgI_2(c, red)	*−25.2*	*−24.3*	*43.*
HgI_2(c, yellow)	*−24.6*		
HgI_2(g)	*−4.1*	*−14.3*	*80.31*
HgI_2(aq, undiss)	−19.2[b]	−17.9[b]	41[b]
HgI_3^-(aq)	−36.7[b]	−35.4[b]	71[b]
HgI_4^{2-}(aq)	−56.4[b]	−50.5[b]	85[b]
HgI(OH)(aq, undiss)		−41.4[121]	
HgICl(aq)		−30.7[b]	
HgIBr(g)			*76.59*
HgIBr(aq, undiss)		−26.6[b]	
$HgIBr_3^{2-}$(aq)		−80.47[b]	
$HgI_2Br_2^{2-}$(aq)		−71.08[b]	
HgI_3Br^{2-}(aq)		−61.1[b]	
Hg_2I_2(c)	*−29.00*	*−26.53*	*55.8*
HgS(c, red)	−12.9	−11.1	*19.7*[136]
HgS(c, black)	−12.0	−10.6	21.2
$HgSO_4$(c)	*−169.1*	−142	(34)
$HgSO_4$(aq, undiss)		−140.5[b]	
Hg_2SO_4(c)	−177.72	−149.70	47.96[164,165]
HgSe(c)	−10.8[147]	−9.1[147]	22.5[147]
$HgSeO_3$(c)		−67.9[b]	
Hg_2SeO_3(c)		*−71.1*	
HgTe(c)	−8.1[150]	−6.7[150]	25.5[150]
$Hg(N_3)^+$(aq)		112.0[204]	
$Hg(N_3)_2$(aq, undiss)		185.0[204]	
$Hg_2(N_3)_2$(c)	141.5[206]	*178.4*	49.9
$Hg(NO_3)^+$(aq)		12.3[203]	
$Hg(NO_3)_2$ (aq) undiss)		−12.0[203]	
$Hg(NO_2)_4^{2-}$(aq)		−11.2[201]	
$Hg(NH_3)^{2+}$(aq)		21.0[195]	
$Hg(NH_3)_2^{2+}$(aq)	−22.6[b]	2.8[195]	41
$Hg(NH_3)_3^{2+}$(aq)	−45.0[b]	−4.9[195]	62
$Hg(NH_3)_4^{2+}$(aq)	−67.8[b]	−12.3[195]	80
$HgNH_2Br$(c, orthorh)			31.83[131]
$HgNH_2Br$(c, cubic			31.09[131]
$Hg_2(P_2O_7)^{2-}$		*−435.*	
$Hg_2(OH)(P_2O_7)^{3-}$ (aq)		*−481.*	
$Hg_2(P_2O_7)_2^{6-}$(aq)		−883	
$Hg_2(OH)_2(P_2O_7)^{4-}$ (aq)		−525	
$Hg(C_2O_4)$(c)	*−162.1*		
Hg_2CO_3(c)	*−132.3*	*−111.9*	*43.*
$Hg_2(C_2O_4)$(c)		*−141.8*	
$Hg_2(C_2O_4)_2^{2-}$(aq)		−295.0	
$Hg_2(OH)(C_2O_4)^-$ (aq)		*−179.8*	
$Hg(CH_3)$(g)	*40.*		
$Hg(CH_3)_2$(liq)	*14.3*	*33.5*	*50.*
$Hg(CH_3)_2$(g)	*22.56*	*34.9*	*73.*
$Hg(CH_3)(C_2H_5)$ (liq)	*11.1*		
$Hg(C_2H_5)_2$(liq)	*7.2*		
$Hg(C_2H_5)_2$(g)	*18.0*		
Hg biphenyl (c)	67.6[211]		
Hg_2Ac_2(c) (Ac^- = acetate)	−201	−152.99	~74
$Hg(CH_3)Cl$(c)	*−27.8*		
$Hg(CH_3)Cl$(g)	*−12.5*		
$Hg(C_2H_5)Cl$(c)	*−33.3*		
$Hg(C_2H_5)Cl$(g)	*−15.0*		
$HgCl_2 \cdot CH_3OH$(c)	−113.5[d]	−83.1[d]	*58.*
$HgCl_2 \cdot 2CH_3OH$ (c)	−172[241]	−123.0[241]	80[241]
$Hg(CH_3)Br$(c)	*−20.5*		
$Hg(CH_3)Br$(g)	*−4.4*		
$Hg(C_2H_5)Br$(c)	*−25.5*		
$Hg(C_2H_5)Br$(g)	*−7.2*		
$Hg(CH_3)I$(c)	*−10.2*		
$Hg(CH_3)I$(g)	*5.2*		
$Hg(C_2H_5)I$(c)	*−15.7*		
$Hg(C_2H_5)I$(g)	*3.3*		
$Hg(CN)^+$(aq)	53.7[b]	57.0[b]	15.8
Hg(CN)Cl(aq, undiss)		16.1[174]	
Hg(CN)Br(aq, undiss)		20.1[174]	

TABLE Ia (Continued)

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]	
$Hg(CN_2)$(c)	66[209]		
$Hg(CN)_2$(c)	*63.0*		
$Hg(CN)_2$(g)	*91.*		
$Hg(CN)_2$(aq, undiss)	66.3[b]	74.7[b]	38.5
$Hg(CN)_2Cl^-$(aq)		43.7[b]	
$Hg(CN)_3^-$(aq)	94.7[b]	110.8[b]	52.5
$Hg(CN)_3Cl^{2-}$(aq)		*80.*	
$Hg(CN)_3Br^{2-}$(aq)		*85.*	
$Hg(CN)_2(tu)$(aq) (tu = thiourea)	49.3[118]		
$Hg(CN)_2(tu)_2$(aq)	25.1[118]		
$Hg(ONC)_2$(c) (mercuric fulminate)	*64.*		
$Hg(SCN)^+$(aq)		49.3[185,186]	
$Hg(SCN)Cl$(aq, undiss)		8.5[b]	
$Hg(SCN)Br$(aq, undiss)		12.3[b]	
$Hg(SCN)_2$(aq, undiss)	46.7[b]	60.5[185,186]	36
$Hg(SCN)_3^-$(aq)		78.8[185,186]	
$Hg(SCN)_4^{2-}$(aq)	77.8[b]	98.4[185,186]	108
$Hg(OH)(SCN)$(aq, undiss)		110.4[65]	
$Hg(SCN)(CN)_3^{2-}$		132.3[b]	
$Hg(SCN)_2$(c)		54.1[141]	
$Hg(ma)^{2+}$(aq) (ma = methylamine)		32.5	
$Hg(ma)_2^{2+}$(aq)	−13.3[223]	24.9	63.4
$HgCl(ma)^+$(aq)	−35.5[223]	−8.3	40.3
$Hg(gl)^+$(aq) (gl^- = glycinate)		−49.9[b]	
$Hg(gl)_2$(aq, undiss)	−205.6[b]	−137.4[b]	63[b]
$HgCl(gl)$(aq, undiss)	−130.3[b]	−89.9[b]	46[b]
$Hg(en)_2^{2+}$(aq) (en = ethylenediamine)	−16.3[b]		
$HgCl(en)^+$(aq)	−33.9[b]		
Hg_2CrO_4(c)		−149.1[141]	

[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 Hg^{2+}(aq). [c] $HHgO_2^-$(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 H_2O(liq). [d] Based on values tabulated in NBS 270-4, adjusted to take into account our revised ΔH_f° and S° values for $HgCl_2$(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 Hg_2^{2+} ions and that Hg_2^{2+}(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 Hg_3^{2+} (formal +2/3 oxidation state) in $AlCl_3$–NaCl melts[26] and in SO_2(liq).[27] Preparation and structure of $[Hg_{2.86}AsF_6]$ 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 Giauque[30] and Smith and Wolcott.[31] We also note that Douglas, Ball, and Ginnings[32] 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 Giauque[30] from heat capacity and vapor pressure results that they have reviewed.

Vapor pressure measurements (260–360°C) by Spedding and Dye[33] 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 Dye[33] 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 Kaloff[35] 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}
Hg(liq)	*0*	*0*	*76.02*[30,31]
Hg(g)	*61.317*	*31.853*	*174.85*
Hg(aq)	13.93[43]	37.2[43]	−2.1
Hg^{+}(g)	*1074.53*		
Hg^{2+}(g)	*2890.4*		
Hg^{2+}(aq)	170.16[53]	164.703[56]	−36.23[56]
Hg^{3+}(g)	*6192*		
Hg_2(g)	*109*	*68.2*	*287.9*
Hg_2^{2+}(aq)	166.82[56]	153.607[56]	65.77[56]
HgO(c, red, orthorh)	*−90.83*	*−58.555*	*70.29*[51]
HgO(c, yellow, orthorh)	−90.83[53]	−58.450[53]	69.87[53]
HgO(c, red, hexag)	−90.33[53]	−58.325[53]	71.25[53]
HgO(g)			241.8[87]
HgH(g)	238[76,193]	213	219.7[76,193]
$Hg(OH)^{+}$(aq)	−84.5	−52.01[b]	69.0
$Hg(OH)_2$(aq, undiss)	−359.8	−274.5[b]	126.4
$Hg(OH)_3^{-}$(aq)		−427.2[c]	
$HHgO_2^{-}$(aq)		−190.0[b]	
HgF(g)	~2.9	~−18.4[76]	248.28[76]
HgF^{+}(aq)	−159.0[b]	−123.0[b]	−8[b]
Hg_2F_2(c)	−485	−431[77]	(167)
HgCl(g)	83.7	62.8	259.9
$HgCl^{+}$(aq)	−19.7[b]	−5.0[b]	71[b]
$HgCl_2$(c)	−225.9	−180.3	*146.0*
$HgCl_2$(g)	−143.1[124]	−141.8[124]	294.68[76,124]
$HgCl_2$(aq, undiss)	−217.1[b]	−172.8[b]	151[b]
$HgCl_3^{-}$(aq)	−389.5[b]	−308.8[b]	205[b]
$HgCl_4^{2-}$(aq)	−554.8[b]	−446.4[b]	289[b]
HgCl(OH)(aq, undiss)	−288.7[118]	−222.2[118,119]	134
Hg_2Cl_2(c)	−265.579[56,86]	−210.773[56,86]	191.42[56,86]
HgBr(g)	~105[76]	~67[76]	271.5[76]
$HgBr^{+}$(aq)	5.4[b]	9.2[b]	75[b]
$HgBr_2$(c)	*−170.7*	*−153.1*	*172*
$HgBr_2$(g)	−86.6[76]	−113.8[76]	320.12[76]
$HgBr_2$(aq, undiss)	−161.5[b]	−142.7	167[b]
$HgBr_3^{-}$(aq)	−294.1[b]	−259.0[b]	255[b]
$HgBr_4^{2-}$(aq)	−431.8[b]	−370.7[b]	305[b]
HgBr(OH)(aq, undiss)		−207.9[120]	
HgBrCl(g)			*299.4*
HgBrCl(aq, undiss)		−161.5[b]	
Hg_2Br_2(c)	−206.94	−181.084[92,93]	217.6
HgI(g)	132.2[99]	91.6[99]	*281.42*
HgI^{+}(aq)	42.3[b]	40.2[b]	75[b]
HgI_2(c, red)	*−105.4*	*−101.7*	*180*
HgI_2(c, yellow)	*−102.9*		
HgI_2(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]	
$HgI_2Br_2^{2-}$(aq)		−297.40[b]	
HgI_3Br^{2-}(aq)		−255.6[b]	
Hg_2I_2(c)	*−121.34*	*−111.002*	*233.5*
HgS(c, red)	−54.0	−46.4	*82.4*[136]
HgS(c, black)	−50.2	−44.4	88.7
$HgSO_4$(c)	*−707.5*	−594	(142)
$HgSO_4$(aq, undiss)		−587.9[b]	
Hg_2SO_4(c)	−743.58	−626.34	200.66[164,165]
HgSe(c)	−45.2[147]	−38.1[147]	94.1[147]
$HgSeO_3$(c)		−284.1[b]	
Hg_2SeO_3		*−297.5*	
HgTe(c)	−33.9[150]	−28.0[150]	106.7[150]
$Hg(N_3)^{+}$(aq)		468.6[204]	
$Hg(N_3)_2$(aq, undiss)		774.0[204]	
$Hg_2(N_3)_2$(c)	592.0[206]	*746.4*	208.8
$Hg(NO_3)^{+}$(aq)		51.5[203]	
$Hg(NO_3)_2$(aq, undiss)		−50.2[203]	
$Hg(NO_2)_4^{2-}$(aq)		−46.9[201]	
$Hg(NH_3)^{2+}$(aq)		87.9[195]	
$Hg(NH_3)_2^{2+}$(aq)	−94.6[b]	11.7[195]	172
$Hg(NH_3)_3^{2+}$(aq)	−188.3[b]	−20.5[195]	259
$Hg(NH_3)_4^{2+}$(aq)	−283.7[b]	−51.5[195]	335
$HgNH_2Br$(c, orthorh)			133.18[131]
$HgNH_2Br$(c, cubic)			130.08[131]
$Hg_2(P_2O_7)^{2-}$(aq)		*−1820*	
$Hg_2(OH)(P_2O_7)^{3-}$(aq)		*−2012*	
$Hg_2(P_2O_7)_2^{6-}$(aq)		−3694	
$Hg_2(OH)_2(P_2O_7)^{4-}$(aq)		−2197	
$Hg(C_2O_4)$(c)	*−678.2*		
Hg_2CO_3(c)	*−553.5*	*−468.2*	*180*
$Hg_2(C_2O_4)$(c)		*−593.3*	
$Hg_2(C_2O_4)_2^{2-}$(aq)		−1234.3	
$Hg_2(OH)(C_2O_4)^{-}$(aq)		*−752.3*	
$Hg(CH_3)$(g)	*167*		
$Hg(CH_3)_2$(liq)	*59.8*	*140.2*	*209*
$Hg(CH_3)_2$(g)	*94.39*	*146.0*	*305*
$Hg(CH_3)(C_2H_5)$(liq)	*46.4*		
$Hg(C_2H_5)_2$(liq)	*30.1*		
$Hg(C_2H_5)_2$(g)	*75.3*		
Hg biphenyl (c)	282.8[211]		
Hg_2Ac_2(c) (Ac^{-} = acetate)	−841	−640.11	~310
$Hg(CH_3)Cl$(c)	*−116.3*		
$Hg(CH_3)Cl$(g)	*−52.3*		
$Hg(C_2H_5)Cl$(c)	*−139.3*		
$Hg(C_2H_5)Cl$(g)	*−62.8*		
$HgCl_2 \cdot CH_3OH$(c)	−474.9[d]	−347.7[d]	*243*
$HgCl_2 \cdot 2CH_3OH$(c)	−720[241]	−514.6[241]	335[241]

TABLE Ib[a] (Continued)

Substance	ΔH_f°, kJ mol^{-1}	ΔG_f°, kJ mol^{-1}	S°, J K^{-1} mol^{-1}
$Hg(CH_3)Br(c)$	*−85.8*		
$Hg(CH_3)Br(g)$	*−18.4*		
$Hg(C_2H_5)Br(c)$	*−106.7*		
$Hg(C_2H_5)Br(g)$	*−30.1*		
$Hg(CH_3)I(c)$	*−42.7*		
$Hg(CH_3)I(g)$	*21.8*		
$Hg(C_2H_5)I(c)$	*−65.7*		
$Hg(C_2H_5)I(g)$	*13.8*		
$Hg(CN)^+(aq)$	224.7[b]	238.5[b]	66.1
$Hg(CN)Cl$(aq, undiss)		67.4[174]	
$Hg(CN)Br$(aq, undiss)		84.1[174]	
$Hg(CN)I$(aq, undiss)		121.3[174,175]	
$Hg(CN_2)(c)$	276[209]		
$Hg(CN)_2(c)$	*263.6*		
$Hg(CN)_2(g)$	*381*		
$Hg(CN)_2$(aq, undiss)	277.4[b]	312.5[b]	161.1
$Hg(CN)_2Cl^-$ (aq)		182.8[b]	
$Hg(CN)_3{}^-(aq)$	396.2[b]	463.6[b]	219.7
$Hg(CN)_3Cl^{2-}$ (aq)		*335*	
$Hg(CN)_3Br^{2-}$ (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*		
$Hg(SCN)^+(aq)$		206.3[185,186]	
$Hg(SCN)Cl$(aq, undiss)		35.6[b]	
$Hg(SCN)Br$ (aq, undiss)		51.5[b]	
$Hg(SCN)_2$(aq, undiss)	195.4[b]	253.1[185,186]	151
$Hg(SCN)_3{}^-(aq)$		329.7[185,186]	
$Hg(SCN)_4{}^{2-}$ (aq)	325.5[b]	411.7[185,186]	452
$Hg(OH)(SCN)$ (aq, undiss)		461.9[65]	
$Hg(SCN)(CN)_3{}^{2-}(aq)$		553.5[b]	
$Hg_2(SCN)_2(c)$		226.4[141]	
$Hg(ma)^{2+}(aq)$ (ma = methylamine		136.0	
$Hg(ma)_2{}^{2+}(aq)$	−55.6[223]	104.2	265.3
$HgCl(ma)^+$ (aq)	−148.5[223]	−34.7	168.6
$Hg(gl)^+(aq)$ (gl^- = glycinate)		−208.8[b]	
$Hg(gl)_2$(aq, undiss)	−860.2[b]	−574.9[b]	264[b]
$HgCl(gl)$(aq, undiss)	−545.2[b]	−376.1[b]	192[b]
$Hg(en)_2{}^{2+}(aq)$ (en = ethylenediamine)	−68.2		
$HgCl(en)^+(aq)$	−141.8[b]		
$Hg_2CrO_4(c)$		−623.8[141]	

[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 $Hg^{2+}(aq)$. [c] $HHgO_2{}^-(aq)$ 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 $H_2O(liq)$. [d] Based on values tabulated in NBS 270-4, adjusted to take into account our revised ΔH_f° and S° values for $HgCl_2(c)$.

Most recently, Ambrose and Sprake[36] 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(liq) and Hg(g). It is possible that the higher temperature and pressure results might be used to obtain more information about $Hg_2(g)$.

Hicks[34] has provided a review of vapor pressures and some related properties of mercury.

Hensel and Franck[37] 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 Davis[38] have used an ultrasonic method for investigating thermal expansion and isothermal compressibility from 20 to 90°C and to 2000 bars. Grindley and Lind[39] 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 solubility[43] (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 Voigt[42] 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 Hames[43] 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 xenon[2] to atomic weight 201 g mol^{-1}. On the other hand, the results of Spencer and Voigt[42] correspond to a larger enthalpy of vaporization from aqueous solution and a smaller entropy for Hg(aq) than estimated from properties[2] of monatomic noble gases. Finally, the results of Glew and Hames[43] 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 $\bar{V}^\circ$ of Hg(aq).[44]

Glew and Hames[45] 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 Mains[46] and Spencer and Voigt[47] have investigated solubilities of mercury in a number of organic solvents. Rosenberg and Kay[48] 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 $\Delta G_f^\circ = -13.995$ kcal mol^{-1} for HgO(c, red, orthorhombic). This value is consistent with the oxygen decomposition pressure measurements of Taylor and Hulett[49] and is also supported by electrochemical results as follows. The NBS tabulated[2,29] free energies lead to the cell potential:

$$\mathrm{HgO(c,red)} + \mathrm{H_2(g)} = \mathrm{Hg(liq)} + \mathrm{H_2O(liq)} \quad E^\circ = 0.9256\ \mathrm{V} \quad (1)$$

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:

$$\mathrm{Ag_2O(c)} + \mathrm{Hg(liq)} = 2\mathrm{Ag(c)} + \mathrm{HgO(c,red)} \quad E^\circ = 0.2453\ \mathrm{V} \quad (2)$$

Measurements by Hamer and Craig[50] and by Gregor and Pitzer[52] 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 $\mathrm{Ag_2O(c)}$, we may regard this ΔG_f° of HgO(c,red,orthorhombic) as being well established.

Vanderzee, Rodenburg, and Berg[53] 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 $S^\circ = 16.80$ cal K^{-1} mol^{-1} for HgO(c,red,orthorhombic), which is the value reported by Bauer and Johnston[51] on the basis of their heat capacities. Bauer and Johnston[51] have cited Randall's calculations with decomposition pressure data[49] with results that now lead us to $S^\circ =$ 17.0 cal K^{-1} mol^{-1} for HgO(c,red,orthorhombic). Hamer and Craig[50] 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 $S^\circ = 17.0$ cal K^{-1} mol^{-1} for HgO(c,red,orthorhombic). Other dE°/dT values cited by Hamer and Craig[50] 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 Craig[50] and by Gregor and Pitzer[52] lead to $S^\circ = 17.6$ cal K^{-1} mol^{-1} for HgO(c,red,orthorhombic). Gregor and Pitzer[52] also suggested that a different treatment of the low temperature heat capacity data[51] would lead to $S^\circ > 16.8$ cal K^{-1} mol^{-1} for HgO(c,red,orthorhombic). On the basis of all of these values, it is reasonable to accept $S^\circ = 16.8$ cal K^{-1} 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 $\Delta H_f^\circ = -21.71$ 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 Rossini[54] calculated $\Delta H_f^\circ = -21.3$ kcal mol^{-1} from results of older calorimetric measurements, but adopted $\Delta H_f^\circ = -21.6$ kcal mol^{-1} based on decomposition pressures and dE°/dT results. We now conclude that it is reasonable to accept $\Delta H_f^\circ = -21.71$ 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 $\mathrm{Hg^{2+}(aq)}$ 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 Berg[53] 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 $\Delta C_p^\circ \simeq 0$ 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:

$$\mathrm{HgO(c,red)} + \mathrm{H_2O(liq)} + 2e^- = \mathrm{Hg(liq)} + 2\mathrm{OH^-(aq)}$$

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

The HgO|Hg electrode corresponding to the half-reaction above has proven useful in investigations of alkaline solutions. Thacker[55] 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 $\mathrm{Hg_2^{2+}(aq)}$ and $\mathrm{Hg^{2+}(aq)}$.

V. $\mathrm{Hg_2^{2+}(aq)}$, $\mathrm{Hg^{2+}(aq)}$, and Hydrolyzed Species

For both $\mathrm{Hg_2^{2+}(aq)}$ and $\mathrm{Hg^{2+}(aq)}$ we adopt the ΔG_f° values calculated by Vanderzee and Swanson[56] 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:

$$\mathrm{Hg_2^{2+}(aq)} + 2e^- = 2\mathrm{Hg(liq)} \quad E^\circ = 0.7960\ \mathrm{V} \quad (3)$$

$$2\mathrm{Hg^{2+}(aq)} + 2e^- = \mathrm{Hg_2^{2+}(aq)} \quad E^\circ = 0.9110\ \mathrm{V} \quad (4)$$

$$\mathrm{Hg^{2+}(aq)} + 2e^- = \mathrm{Hg(liq)} \quad E^\circ = 0.8535\ \mathrm{V} \quad (5)$$

$$\mathrm{Hg(liq)} + \mathrm{Hg^{2+}(aq)} = \mathrm{Hg_2^{2+}(aq)} \quad K = 88 \quad (6)$$

In addition to the experimental results already cited[56] in support of these values, we note that McKeown[57] has found $K =$ 90 for equilibrium 6, in excellent agreement with the value above.

Zielen and Sullivan[58] have carried out measurements on the $\mathrm{Hg_2^{2+}}$|Hg and $\mathrm{Hg^{2+}}$|$\mathrm{Hg_2^{2+}}$ 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 Voigt[40] have discussed previous work and set a limit on possible dissociation of aqueous mercurous ions as indicated by

$$Hg_2^{2+}(aq) = 2Hg^+(aq) \quad K < 10^{-7}$$

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

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

$$HgO(c,red) + H_2O(liq) = Hg^{2+}(aq) + 2OH^-(aq)$$

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

This K_{sp} value is in good agreement with that reported by Feitknecht and Schindler[59] 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 $K_{sp} = 0.53 \times 10^{-26}$. The difference between this K_{sp} and the calculated value above corresponds to a total discrepancy of 1.0 kcal mol^{-1} in $\Delta G_f°$ values for HgO(c,red) and $Hg^{2+}(aq)$. Although there are only small uncertainties associated with the measured solubilities, there is substantial uncertainty associated with interpretation[60] in terms of $Hg^{2+}(aq)$, $Hg(OH)^+(aq)$, etc. Thus it is reasonable to accept the calculated $K_{sp} = 2.8 \times 10^{-26}$ as the "best" value and to regard the quoted K_{sp} from solubilities as providing approximate confirmation of the tabulated free energies of HgO(c,red) and $Hg^{2+}(aq)$.

We also have $pK_{sp} = 26.0$ (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 Hg(II) we adopt the following equilibrium constants and also the $\Delta G_f°$ values listed in Table I:

$$Hg^{2+}(aq) + H_2O(liq) = Hg(OH)^+(aq) + H^+(aq) \quad (7)$$

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

$$Hg(OH)^+(aq) + H_2O(liq) = Hg(OH)_2(aq) + H^+(aq) \quad (8)$$

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

$$Hg(OH)_2(aq) + OH^-(aq) = Hg(OH)_3^-(aq) \quad (9)$$

$$K = 0.16$$

$$HgO(c,red) + H_2O(liq) + OH^-(aq) = Hg(OH)_3^-(aq) \quad (10)$$

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

These equilibrium constants are consistent with the $\Delta G_f°$ values in NBS 270-4, but our tabulated $\Delta G_f°$ values are slightly different from theirs because our $\Delta G_f°$ for $Hg^{2+}(aq)$ differs from theirs. It should also be recognized that $Hg(OH)_3^-(aq)$ (as above) and $HHgO_2^-(aq)$ (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 investigations[60-66] of the solubility of HgO(c,red) and hydrolysis of Hg(II) solutions.

Johansson's[67] X-ray investigations of aqueous $Hg(ClO_4)_2$ 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 Hg–O distance. There is X-ray evidence for polynuclear species, which have also been invoked by Ahlberg[62] in interpretation of hydrolysis data.

We now turn to consideration of $\Delta H_f°$ and $S°$ values for the aqueous species whose free energies have been discussed above.

For $Hg^{2+}(aq)$ we adopt $\Delta H_f° = 40.67$ kcal mol^{-1} from the calorimetric $\Delta H°$ of solution of HgO(c,red) in $HClO_4(aq)$ measured by Vanderzee, Rodenburg, and Berg.[53] Similar measurements by earlier investigators[68,69] lead to a $\Delta H_f°$ value (identical with that listed in NBS 270-4) that is 0.2 kcal mol^{-1} more endothermic than our adopted value. Combination of our adopted $\Delta H_f°$ with the $\Delta G_f°$ cited previously[56] leads to $S° = -8.6_6$ cal K^{-1} mol^{-1} for $Hg^{2+}(aq)$ as also calculated by Vanderzee and Swanson.[56]

For $Hg_2^{2+}(aq)$ we adopt $\Delta H_f° = 39.87$ kcal mol^{-1} and $S° = 15.7_2$ cal K^{-1} 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 $Hg_2Cl_2(c)$ with the $\Delta H_f°$ of $Hg_2Cl_2(c)$ that we consider in the next section. Vanderzee and Swanson[56] have also combined their $S°$ for $Hg^{2+}(aq)$ with the $\Delta S°$ for reaction 6 that they have derived from the results of Schwarzenbach and Anderegg[70] to obtain a value of $S°$ for $Hg_2^{2+}(aq)$ that is very close to the adopted value.

There are several other paths to $\Delta H_f°$ and $S°$ of $Hg_2^{2+}(aq)$. For example, measurements by McKeown[57] lead to $\Delta S°$ for reaction 6 and thence to $S° = 16.4$ cal K^{-1} mol^{-1} for $Hg_2^{2+}(aq)$. We also use the potentials (20–35°C) reported by Pan, Chang, and Hsin[71] for the couple represented by (3) to calculate $S° = 13.2$ cal K$^-$ mol^{-1} for $Hg_2^{2+}(aq)$. Results obtained by Galloway[72] and Read[73] for $\Delta S°$ of dissolution of $Hg_2Cl_2(c)$ and $Hg_2Br_2(c)$ as discussed in the next section of this review lead to $S° = 17$ and 18 cal K$^-$ mol^{-1} for $Hg_2^{2+}(aq)$. Using data on the solubility of $Hg_2SO_4(c)$ from Sharma and Prasad[74] as discussed in section IX, we obtain $S° = 20$ cal K^{-1} mol^{-1} for $Hg_2^{2+}(aq)$, which is the same as the value listed in NBS 270-4.

There are $\Delta H°$ and $\Delta S°$ values for hydrolysis of $Hg^{2+}(aq)$ from the d 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 $\Delta H_f°$ and $S°$ values listed in Table I for $Hg(OH)^+(aq)$ and $Hg(OH)_2$(aq,undissociated). There are also enthalpy data (3 M ClO_4^-) available[75] for $Hg_2(OH)^{3+}(aq)$ and $Hg_2(OH)_2^{2+}(aq)$. Both of these species and also $Hg_4(OH)_3^{5+}(aq)$ were postulated by Ahlberg[62] in connection with equilibrium studies.

VI. Mercury(I) Halides

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

For $Hg_2F_2(c)$ we have $\Delta G_f° = -102.2$ kcal mol^{-1} from the JANAF tables,[76] based on cell measurements of Koerber and DeVries,[77] and $\Delta G_f° = -104.1$ 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 $\Delta G_f° = -103$ kcal mol^{-1} and combine with our estimated $S° = (40)$ cal K^{-1} mol^{-1} to obtain $\Delta H_f° = -116$ kcal mol^{-1} for $Hg_2F_2(c)$.

Combination of the NBS 270-4 $\Delta G_f°$ for $Hg_2Cl_2(c)$ with the $\Delta G_f°$ for $Cl^-(aq)$[2] leads to $E° = 0.26814$ V for the $Hg_2Cl_2|Hg$ couple. This calculated potential is in good agreement with the reported results of a considerable number of careful investigations.[78-85] Ahluwalia and Cobble[86] and Vanderzee and Swanson[56] have analyzed many of these results and have chosen $E° = 0.268155$ V. On the basis of these analyses and our own recalculations, we adopt the following potential:

$$Hg_2Cl_2(c) + 2e^- = 2Hg(liq) + 2Cl^-(aq) \quad E° = 0.26816\ V$$

This potential corresponds to $\Delta G_f° = -50.376$ kcal mol^{-1} for $Hg_2Cl_2(c)$ and is the value adopted for Table I.

We use the $Hg_2Cl_2|Hg$ potential above with the $Hg_2^{2+}|Hg$ potential given earlier to calculate the solubility product:

$$Hg_2Cl_2(c) = Hg_2^{2+}(aq) + 2Cl^-(aq) \quad K_{sp} = 1.42 \times 10^{-18}$$

Most K_{sp} values quoted in the literature for $Hg_2Cl_2(c)$ are derived from potentials (or related free energies) as outlined above and therefore are not a meaningful check on this value. But Galloway[72] has made independent measurements that lead to $K_{sp} = 1.49 \times 10^{-18}$. The good agreement between this "direct" value and that derived from $E°$ values (or related $\Delta G_f°$ values) offers convincing confirmation of the various tabulated free energies.

The only low-temperature heat capacity data available for $Hg_2Cl_2(c)$ are the old (1911 and 1913) results of Pollitzer that have led Kelley and King[87] to $S° = 46.0 \pm 0.5$ cal K^{-1} 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" $\Delta H_f°$ and $S°$ for $Hg_2Cl_2(c)$ as described below.

Ahluwalia and Cobble[86] and Vanderzee and Swanson[56] have analyzed $E°$ values at several temperatures in terms of the cell reaction

$$H_2(g) + Hg_2Cl_2(c) = 2Hg(liq) + 2H^+(aq) + 2Cl^-(aq)$$

Both analyses are in agreement with $\Delta H° = -16.429$ kcal mol^{-1} and $\Delta S° = -13.62$ cal K^{-1} 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 $\Delta H°$ and $\Delta S°$ values quoted above. These values lead us to $\Delta H_f° = -63.47_5$ kcal mol^{-1} and $S° = 45.7_5$ cal K^{-1} mol^{-1} for $Hg_2Cl_2(c)$ as listed in Table I. This $\Delta H_f°$ was used by Vanderzee and Swanson[56] in their evaluation of the thermodynamic properties of $Hg_2^{2+}(aq)$.

Galloway's[72] K_{sp} values for $Hg_2Cl_2(c)$ at seven temperatures (15–45°C) lead to $\Delta H°$ and $\Delta S°$ values that are in reasonable arreement with $\Delta H_f°$ and $S°$ values we have assigned to $Hg_2Cl_2(c)$ and $Hg_2^{2+}(aq)$.

We emphasize that a third law entropy of $Hg_2Cl_2(c)$ 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 $E° = 0.13924$ V for the $Hg_2Br_2|Hg$ potential. On the basis of an average of the results of Gupta, Hills, and Ives[92] and Leuschke and Schwabe[93] (recalculated using our $E°$ for $Hg_2Cl_2|Hg$), we adopt the following:

$$Hg_2Br_2(c) + 2e^- = 2Hg(liq) + 2Br^- \quad E° = 0.13920\ V$$

This potential corresponds [using $\Delta G_f°$ for $Br^-(aq)$ from NBS 270-3] to $\Delta G_f° = -43.280$ kcal mol^{-1} for $Hg_2Br_2(c)$ as in Table I.

We also note that Dakin and Ewing[94] and Larson[95] have measured potentials of cells in which the reaction is

$$2Ag(c) + Hg_2Br_2(c) = 2AgBr(c) + 2Hg(liq)$$

and obtained $E° = 0.06804$ and 0.06835 V, respectively. Combination of these potentials with $\Delta G_f°$ for AgBr(c) in NBS 270-4 leads to $E° = 0.1413$ and 0.1416 V, respectively, for the $Hg_2Br_2|Hg$ potential. But we can also combine these measured potentials with $E° = 0.07106$ V for $AgBr|Ag$ from Hetzer, Robinson, and Bates[96] to obtain $E° = 0.1391$ and 0.1394 V, respectively, in better agreement with our adopted value.

We use our free energies to calculate the solubility product:

$$Hg_2Br_2(c) = Hg_2^{2+}(aq) + 2Br^-(aq) \quad K_{sp} = 6.22 \times 10^{-23}$$

Several previously tabulated solubility products for $Hg_2Br_2(c)$ have been calculated from $\Delta G_f°$ values or potentials similar to those cited above and do not constitute an independent check on our K_{sp}. But Read[73] has independently found $K_{sp} = 6.43 \times 10^{-23}$, which is in satisfactory agreement with our value.

The NBS 270-4 and Kelley and King[87] list $S° = 52$ and 52.0 cal K^{-1} mol^{-1}, respectively, for $Hg_2Br_2(c)$. 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 $S° = 52.0$ cal K^{-1} mol^{-1} for $Hg_2Br_2(c)$. The results of Larson[95] 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 $\Delta G_f°$ and $S°$ for $Hg_2Br_2(c)$ to obtain the $\Delta H_f°$ that we list in Table I.

The $Hg_2Br_2|Hg$ electrode has been investigated[97] in aqueous alcohol systems.

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

$$Hg_2I_2(c) + 2e^- = 2Hg(liq) + 2I^-(aq) \quad E° = -0.0405\ V$$

$$Hg_2I_2(c) = Hg_2^{2+}(aq) + 2I^-(aq) \quad K_{sp} = 5.16 \times 10^{-29}$$

These values are consistent with the cell data of Bates and Vosburgh.[98] The $\Delta H_f°$ for $Hg_2I_2(c)$ listed in NBS 270-4 is consistent with the results of older calorimetric and electrochemical results that have been reviewed by Bichowsky and Rossini[54] and in the JANAF tables.[76] The substantial uncertainties in these latter values could be considerably reduced by a third law entropy for $Hg_2I_2(c)$.

For HgCl(g) we have thermodynamic properties listed in NBS 270-4 and the JANAF tables[76] that are in reasonable agreement. The properties of HgI(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 HgBr(g) we have approximate $\Delta H_f°$ and $\Delta G_f°$ values and a more accurate $S°$ from the JANAF tables.[76] Entropies for these HgX(g) compounds are also given by Kelley and King.[87] All of the $\Delta H_f°$ values are derived from dissociation energies and all of the entropies are calculated from molecular constants.

VII. Mercury(II) Halides

The $\Delta G_f°$ values for aqueous mercuric halide species listed in NBS 270-4 in combination with $\Delta G_f°$ 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 $\Delta H_f°$ 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 Woodward[113] have presented spectroscopic evidence for existence of $Hg_2I^{3+}(aq)$ in moderately concentrated solutions.

The NBS 270-4 $\Delta G_f°$ 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 $HgBr_4^{2-}(aq) + nI^-(aq) = HgBr_{4-n}I_n^{2-}(aq) + nBr^-(aq)$

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:

$$HgCl_2(aq) + HgBr_2(aq) = 2HgClBr(aq) \quad K = 21$$

$$HgCl_2(aq) + HgI_2(aq) = 2HgICl(aq) \quad K = 41$$

$$HgBr_2(aq) + HgI_2(aq) = 2HgIBr(aq) \quad K = 7.6$$

These values are in fair agreement with those reported by Marcus[114] and Spiro and Hume.[115] All of the above equilibrium constants are significantly greater than the statistical value of 4.

The NBS 270-4 $\Delta G_f°$ values also lead to the equilibrium constants for successive substitution of I^- for Br^- in $HgBr_4^{2-}(aq)$, as summarized in Table III. All four of these equilibrium constants are in excellent agreement with the results of Spiro and Hume[116] for these reactions. Also, the equilibrium constant for $n = 4$ is in excellent agreement with independently determined stability constants for $HgBr_4^{2-}(aq)$ and $HgI_4^{2-}(aq)$.

We are unable to reconcile the unclear d ln K/dT results reported by Eliezer[117] for mixed halides with NBS 270-4 $\Delta H_f°$ and $S°$ values so our listings in Table I are limited to $\Delta G_f°$ values for these mixed halide species.

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

$$HgCl_2(aq) + 2OH^-(aq) = Hg(OH)_2(aq) + 2Cl^-(aq) \quad (11)$$

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

$$HgCl_2(aq) + 2H_2O(liq) = Hg(OH)_2(aq) + 2H^+(aq) + Cl^-(aq) \quad (12)$$

The first equilibrium constant is larger than $K = 7.2 \times 10^7$ reported by Partridge, Izatt, and Christensen[118] and the second is larger than $K = 2.5 \times 10^{-20}$ for 1 M ClO_4^- 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 $HgCl_2(aq)$ and $Hg(OH)_2(aq)$. We retain the $\Delta G_f°$ 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 $HgCl_2(aq)$.

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

$$HgCl_2(aq) + OH^-(aq) = HgCl(OH)(aq) + Cl^-(aq) \quad (13)$$

We use this K value in calculating the $\Delta G_f°$ for HgCl(OH)(aq) listed in our Table I. Because of discrepancies noted above, this $\Delta G_f°$ may not have quite the right relationship to that tabulated for $Hg(OH)_2(aq)$.

The $\Delta H_f°$ values in NBS 270-4 and NBS 270-3 lead to a calculated $\Delta H° = -3.2$ kcal mol^{-1} for reaction 11, while the calorimetric measurements of Partridge, Izatt, and Christensen[118] have led to $\Delta H° = -2.5$ 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 $\Delta H_f°$ values [except as required because of our changed properties of $Hg^{2+}(aq)$]. But we do use the results of Partridge, Izatt, and Christensen[118] for reaction 13 for calculation of both $\Delta H_f°$ 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 Leden[120] have investigated the equilibrium

$$Hg^{2+}(aq) + Br^-(aq) + H_2O(liq) = HgBr(OH)(aq) + H^+(aq)$$

in 3 and 0.5 M $ClO_4^-(aq)$ solution and have reported $K = 7.9 \times 10^5$ and $K = 4.8 \times 10^5$ for these solutions. Similarly, Ahlberg[121] has found $K = 7.9 \times 10^8$ for

$$Hg^{2+}(aq) + I^-(aq) + H_2O(liq) = HgI(OH)(aq) + H^+(aq)$$

in 0.5 M $ClO_4^-(aq)$ solution. Our $\Delta G_f°$ 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 DMSO[122] and in acetonitrile,[123] with the latter investigation including evaluation of the $Hg^{2+}|Hg_2^{2+}$ and $Hg_2^{2+}|Hg$ potentials and the equilibrium constant for disproportionation of Hg_2^{2+} in this solvent.

Johnson, Silva, and Cubicciotti[124] have made extensive measurements of the vapor pressure of $HgCl_2(liq)$ 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 Johnson[125] reported results of their high-temperature calorimetric measurements on $HgCl_2$. These papers, which are admirable examples of high quality measurements and full thermodynamic treatment of resulting data, are a reliable source of $\Delta H°_{298}$ and $\Delta S°_{298}$ of vaporization of $HgCl_2(c)$. Combining their quoted $S°_{298} = 70.43$ cal K^{-1} mol^{-1} for $HgCl_2(g)$ (calculated from molecular constants) with their $\Delta S°_{298}$ of vaporization leads to $S°_{298} = 34.9$ cal K^{-1} mol^{-1} for $HgCl_2(c)$, 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 $\Delta H_f° = -53.6$ kcal mol^{-1} for $HgCl_2(c)$ listed in NBS 270-4 is consistent with old enthalpy of reaction data[54] and our adopted $\Delta H_f°$ of $Hg_2Cl_2(c)$. Combination of this $\Delta H_f°$ and the $S°$ cited above leads to the NBS 270-4 $\Delta G_f° = -42.7$ kcal mol^{-1} for $HgCl_2(c)$. There are two other routes to $\Delta H_f°$ and $\Delta G_f°$ of $HgCl_2(c)$, 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 $HgCl_2(aq)$ with much smaller concentrations of other species such as $HgCl^+(aq)$, etc. Taking the activity coefficient of $HgCl_2(aq)$ to be unity in combination with the solubility and the previously adopted $\Delta G_f°$ of $HgCl_2(aq)$ leads us to $\Delta G_f° = -42.2$ kcal mol^{-1} for $HgCl_2(c)$. Combination of this value with the entropy then leads to $\Delta H_f° = -53.1$ kcal mol^{-1} for $HgCl_2(c)$.

Still another path involves the enthalpy of solution of $HgCl_2$(c) reported by Abraham, Irving, and Johnston[128] in combination with the tabulated $\Delta H_f°$ of $HgCl_2$(aq), which now leads us to calculate $\Delta H_f° = -55.4$ kcal mol^{-1} and thence $\Delta G_f° = -44.5$ kcal mol^{-1} for $HgCl_2$(c).

The best we can do now is to adopt averages of the values quoted above: $\Delta H_f° = -54.0$ and $\Delta G_f° = -43.1$ kcal mol^{-1} for $HgCl_2$(c).

There have been several investigations[126-128] of the thermodynamics of $HgCl_2$ in various aqueous alcohol solvent systems. Eliezer and Adida[129] have measured solubilities of $HgCl_2$(c) and $HgBr_2$(c) in several organic solvent systems at several temperatures.

Yosim and Mayer[130] 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 $\Delta H \simeq 11$ kcal mol^{-1} for fusion of Hg_2Cl_2(c).

Our tabulated $\Delta H_f°$ and $\Delta G_f°$ for $HgCl_2$(g) are consistent with our selections for $HgCl_2$(c) and the thermodynamics of vaporization previously cited.[124,125]

The NBS 270-4 $\Delta G_f°$ of $HgBr_2$(c) is in excellent agreement with our tabulated $\Delta G_f°$ for $HgBr_2$(aq) and the solubility of $HgBr_2$(c). The $\Delta H_f°$ listed in NBS 270-4 for $HgBr_2$(c) is in agreement with old calorimetric results.[54] We combine these values to obtain our tabulated $S° = 41$ cal K^{-1} mol^{-1}, which is the same as the value listed in NBS 270-4 for $HgBr_2$(c). We also have $S°$ of $HgBr_2$(g) calculated from molecular constants.[76,87] Combination of this $S°$ with $\Delta S°$ of vaporization[76] again leads to $S° = 41$ cal K^{-1} mol^{-1} for $HgBr_2$(c). We obtain $\Delta H_f°$ and $\Delta G_f°$ for $HgBr_2$(g) from corresponding quantities for $HgBr_2$(c) and the thermodynamics of vaporization.[76]

The stable form of $HgNH_2Br$(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 Staveley[131] 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 cal K^{-1} mol^{-1}, which we list in Table I. Similar treatment of heat capacities of the cubic form leads to $S° = S_0 + 31.07$ cal K^{-1} 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 $S° = 31.11$ cal K^{-1} 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 suggested[131] that S_0 should be about 1.6 cal K^{-1} mol^{-1} if the "random walk disorder" persisted to the absolute zero.

The NBS 270-4 $\Delta H_f°$ values for both the red and yellow forms of HgI_2(c) are in agreement with the results of old calorimetric measurements.[54] For HgI_2(g) the NBS 270-4 $S°$ is in agreement with values calculated[76,87] from molecular constants. The thermodynamics of vaporization[76] lead to $S°$ and $\Delta G_f°$ of HgI_2(c,red) and to $\Delta H_f°$ and $\Delta G_f°$ of HgI_2(g) in agreement with the values listed in NBS 270-4. There is only fair agreement between the solubility of HgI_2(c) and the tabulated $\Delta G_f°$ values for HgI_2(c) and HgI_2(aq).

Morris and Whitlock[132] have investigated the distribution of HgI_2 between water and CCl_4, while Kettrup and Specker[133] 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 Tunell[134] and Kullerud[135] 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 $S° = 19.7$ cal K^{-1} mol^{-1} for HgS(c,red), which is the value reported by King and Weller[136] on the basis of their heat capacity measurements (52–297 K). We adopt this value.

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

The NBS 270-4 $\Delta H_f°$ and $\Delta G_f°$ values for HgS(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 HgS(c,red) and HgS(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 Munir[139] cast doubt on some of the results of Goldfinger and Jeunehomme[137] and may be interpreted to indicate that both $\Delta H_f°$ and $\Delta G_f°$ for HgS(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 $\Delta G_f°$ of HgS(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 $\Delta G_f°$ values with $\Delta G_f°$ for H_2S(aq) from NBS 270-3 to calculate the following potentials:

$$\text{HgS(c,red)} + 2\text{H}^+\text{(aq)} + 2e^- = \text{Hg(liq)} + \text{H}_2\text{S(aq)}$$

$$E° = -0.096 \text{ V}$$

$$\text{HgS(c,black)} + 2\text{H}^+\text{(aq)} + 2e^- = \text{Hg(liq)} + \text{H}_2\text{S(aq)}$$

$$E° = -0.085 \text{ V}$$

We use our $\Delta G_f°$ of HgS(c,black) with our $\Delta G_f°$ of Hg^{2+}(aq) and the $\Delta G_f°$ for S^{2-}(aq) from NBS 270-3 to calculate $K_{sp} = 2 \times 10^{-52}$. It is important to recognize that this calculated K_{sp} is tied to the equilibrium constant for the second ionization of H_2S(aq), which in this case means $K = 1 \times 10^{-13}$ that is consistent with NBS 270-3[2] free energies for HS^-(aq) and S^{2-}(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 H_2S(aq) nor the K_{sp} of HgS(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 Giggenbach[143] that the second ionization constant of H_2S(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 S^{2-}(aq) must be changed and that all calculations that involve the concentration or activity of S^{2-}(aq) in solution must be revised. Because the new[143] and older[141,142] ionization constant determinations have been done "reasonably," there is no immediately satisfactory way to resolve this question.

Schwarzenbach and Widmer[144] and more recently Barnes, Romberger, and Stemprok[145] 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 HgS_2^{2-}(aq), $Hg(HS)_2$(aq), $HgS(HS)_2^{2-}$(aq), etc. Because of combined uncertainties in the free energies of HgS(c,red) and HgS(c,black) and in the second ionization constant of H_2S(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 Barnes[146] have made use of results of solubility studies in planning a method for hydrothermal growth of single crystals of HgS(c,red).

Ratajczak and Terpilowski[147] have made electrochemical measurements that lead to $\Delta G_f^\circ = -9.1 \pm 0.5$ kcal mol^{-1}, $\Delta H_f^\circ = -10.8 \pm 0.7$ kcal mol^{-1}, and $S^\circ = 22.5 \pm 0.9$ cal K^{-1} mol^{-1} for HgSe(c). Combination of this ΔG_f° with our ΔG_f° for Hg^{2+}(aq) and the NBS 270-3 ΔG_f° for Se^{2-}(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 Niedrach[148] from results of their polarographic measurements and ionization constants for H_2Se(aq) that were slightly different from those that are consistent with the NBS 270-3 free energies of H_2Se(aq), HSe^-(aq), and Se^{2-}(aq). More recently, solubility measurements by Mehra and Gubeli[149] have led these workers to report $K_{sp} = 2.5 \times 10^{-57}$ on the basis of ionization constants for H_2Se(aq) that are significantly different than those that are consistent with the NBS 270-3[2] free energies. Combination of their ionization constants with their reported K_{sp} leads us to calculate $\Delta G_f^\circ = -11.9$ kcal mol^{-1} for HgSe(c). We adopt the thermodynamic properties for HgSe(c) from Ratajczak and Terpilowski,[147] but note that a free energy from Mehra and Gubeli[149] may be "better" for the mercuric selenide that is precipitated from aqueous solution.

For HgTe(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 HgSe(c) and HgTe(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 HgSe(g) and HgTe(g).

IX. Hg_2SO_4 and $HgSO_4$

The ΔG_f° values listed in NBS 270-4 for Hg_2SO_4(c) and in NBS 270-3 for SO_4^{2-}(aq) correspond to $E^\circ = 0.6153$ V for the $Hg_2SO_4|Hg$ couple and with our ΔG_f° for Hg_2^{2+}(aq) to $K_{sp} = 8.0 \times 10^{-7}$ for Hg_2SO_4(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-Jones[160] have carried out very thorough emf measurements and calculations that lead to $E^\circ = 0.6125$ V. Other emf measurements by Sharma and Prasad[161] have led to $E^\circ = 0.6135$ V. The "third law" analysis of Gardner, Mitchell, and Cobble[162] suggests that $E^\circ = 0.6125$ V is the "best" value for the $Hg_2SO_4|Hg$ couple. We also have $K_{sp} = 6.8 \times 10^{-7}$ from the solubility measurements of Brown and Land,[163] and thence a calculated $E^\circ = 0.6136$ V.

As Covington, Dobson, and Wynne-Jones[160] have pointed out, evaluation of the standard potential from measured potentials depends on the ionization constant chosen for HSO_4^-(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:

$$Hg_2SO_4(c) + 2e^- = 2Hg(liq) + SO_4^{2-}(aq) \quad E^\circ = 0.613 \text{ V}$$

$$Hg_2SO_4(c) = Hg_2^{2+}(aq) + SO_4^{2-}(aq) \quad K_{sp} = 6.5 \times 10^{-7}$$

Our $\Delta G_f^\circ = -149.70$ kcal mol^{-1} for Hg_2SO_4(c) is consistent with these values.

Heat capacity measurements by Brackett, Hornung, and Hopkins[164] and by Papadopolos and Giauque[165] have led to a reliable $S^\circ_{298} = 47.96$ cal K^{-1} mol^{-1} for Hg_2SO_4(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-Jones[158] and Sharma and Prasad[161] 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 Hg_2SO_4(c) and combine with our ΔG_f° to obtain the ΔH_f° listed in Table I.

The ΔH_f° of $HgSO_4$(c) listed in NBS 270-4 is consistent with old calorimetric results[54] and is adopted for our Table I.

The ΔG_f° values for $HgSO_4$(aq) and Hg^{2+}(aq) in NBS 270-4 and the ΔG_f° for SO_4^{2-}(aq) in NBS 270-3 lead to $K = 26$ for

$$Hg^{2+}(aq) + SO_4^{2-}(aq) = HgSO_4(aq,undissoc)$$

The same value has been reported by Posey and Taube[166] for solutions with ionic strength 0.32 *M*. In the absence of activity coefficients, we accept this *K* and the related ΔG_f° for $HgSO_4$(aq), which differs slightly from that in NBS 270-4 because of the difference in ΔG_f° values for Hg^{2+}(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 Eatough.[168] The second, third, and fourth constants are in reasonable agreement with polarographic results ($\mu = 2.0$ *M* and 30°C) of Newman, Cabral, and Hume.[169]

There have been several claims[170] concerning complex ions such as $Hg(CN)_n^{2-n}$(aq) with $n > 4$, but it now appears certain from the spectroscopic work of Ashurst, Finkelstein, and Goold[171] that these earlier reports are mistaken.

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

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

Reaction	K	
	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
$HgL_2(ag) + L^-(aq) = HgL_3^-(aq)$	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] $\Delta H°$ values for formation of $Hg(CN)_4^{2-}(aq)$ from $Hg(CN)_3^-(aq)$ and from $Hg^{2+}(aq)$ range from 0.3 to 4.3 kcal mol^{-1} more exothermic than those calculated from the NBS 270-4 $\Delta H_f°$ values. Our adopted $\Delta H_f°$ 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 $\Delta H_f°$ of $Hg^{2+}(aq)$, while our $\Delta H_f°$ for $Hg(CN)_4^{2-}(aq)$ 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 Gaizer[174] have investigated equilibria of type

$$HgX_2(aq) + Hg(CN)_2(aq) = 2HgX(CN)(aq)$$

and have reported K = 8.46 for X = Cl^-, K = 1.94 for X = Br^-, and K = 0.11 for X = I^-. More recently, Coleman et al.[175] have reported K = 0.14 for the reaction with X = I^-. We use these results in calculating our tabulated $\Delta G_f°$ 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:

$$Hg(CN)_2(aq) + Cl^-(aq) = Hg(CN)_2Cl^-(aq) \quad K = 0.5$$

$$Hg(CN)_3^-(aq) + Cl^-(aq) = Hg(CN)_3Cl^{2-}(aq) \quad K = 0.3$$

$$Hg(CN)_2Cl^-(aq) + CN^-(aq) = Hg(CN)_3Cl^{2-}(aq) \quad K = 3.3 \times 10^3$$

$$Hg(CN)_3^-(aq) + Br^-(aq) = Hg(CN)_3Br^{2-}(aq) \quad K = 4.2$$

These values are in reasonable agreement with the equilibrium constants reported by Newman and Hume[176] and by Agrawal, Vishnu, and Mehrotra[177] 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]

$$Hg(CN)_2(aq) + tu(aq) = Hg(CN)_2(tu)(aq) \quad K = 119$$

$$Hg(CN)_2(aq) + 2tu(aq) = Hg(CN)_2(tu)_2(aq) \quad K = 441$$

These values and related $\Delta H°$ values[178] 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–ethanol[180] and water–formamide[179] systems, with the latter investigation including results for 100% formamide.

Following the initial observation by Birk and Espenson[181] of the "unexpected" stability of a species formed by association of $Hg^{2+}(aq)$ with $Cr(CN)^{2+}(aq)$, there have been several investigations of this and related reactions. For example, from Frank and Anson[182] we have the following:

$$Hg^{2+}(aq) + Cr(CN)^{2+}(aq) = Hg(CN)Cr^{4+}(aq) \quad K = 3 \times 10^7$$

$$Hg(CN)Cr^{4+}(aq) + Cr(CN)^{2+}(aq) = Hg(CN)_2Cr_2^{6+}(aq) \quad K = 4 \times 10^7$$

We also have equilibrium constants for interaction of $Hg(CN)_2(aq)$ with $Fe(CN)_6^{4-}(aq)$, $Mo(CN)_8^{3-}(aq)$, and $Ru(CN)_6^{4-}(aq)$ from the work of Beck and Porzsolt.[183]

Cell measurements by Rock[184] have led to a reported K_{sp} = 1.9×10^{-37} for mercurous cobalticyanide, $(Hg_2)_3[Co(CN)_6]_2(c)$. This reported K_{sp} was based in part on $E°$ = 0.789 V (rather than $E°$ = 0.796 V cited in our section V) for the $Hg_2^{2+}|Hg$ potential. Recalculation of the reported[184] results with this latter potential now leads to a new K_{sp} = 3.7×10^{-38}. Rock[184] has pointed out that the solid phase referred to as $(Hg_2)_3[Co(CN)_6]_2(c)$ 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_{sp} = 1.1×10^{-12} for $(Hg_2)_2[Fe(CN)_6](c)$ and K_{sp} = 8.5×10^{-21} for $(Hg_2)_3[Fe(CN)_6]_2(c)$, as quoted by Sillen.[141] Sillen[141] has also cited K_{sp} = 5×10^{-40} for $Hg_2(CN)_2(c)$, from which we calculate our tabulated $\Delta G_f°$ 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 Morayama[185] and more recently by Ciavatta and Grimaldi.[186] Our $\Delta G_f°$ 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 $\Delta H_f°$ values are based on the calorimetric results of Ahrland and Kullberg.[187] These values are in reasonable agreement with earlier results, which have been reviewed by Ahrland and Kullberg.[187]

Ciavatta, Grimaldi, and Mangone[65] have interpreted their results of investigations of hydrolysis of mercuric thiocyanate solutions in terms of the following:

$$Hg^{2+}(aq) + SCN^-(aq) + H_2O(liq) = Hg(OH)(SCN)(aq) + H^+(aq)$$

$$K = 5 \times 10^5$$

Falk and Linck[188] have reported equilibrium constants for reaction between $Hg^{2+}(aq)$ and $Co(SCN)^{2+}(aq)$. Armor and Haim[189] have reported equilibrium constants at several temperatures (and derived $\Delta H°$ and $\Delta S°$ values) for the reaction

$$Hg^{2+}(aq) + Cr(NCS)^{2+}(aq) = Hg(SCN)Cr^{4+}(aq) \quad K = 1.66 \times 10^4$$

Sillen[141] has listed solubility products for $Hg_2(SCN)_2(c)$ from which we select K_{sp} = 2×10^{-20} and calculate the $\Delta G_f°$ that is listed in Table I. Sillen[141] has also listed solubility products for compounds of type $M[Hg(SCN)_4]$ in which M represents Co^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}. Because of disagreements between the results of different investigators and uncertainties about the state of hydration of the solid phases, we do not tabulate $\Delta G_f°$ values for any of these compounds.

Czakis-Sulikowska[190] has reported stability constants for mixed complexes involving SCN^- with NO_2^-, Cl^-, Br^-, and I^-. Some related equilibrium constants have also been reported by Yakhkind and Gyunner.[191] In an earlier paper these latter workers report[192] equilibrium constants for formation of $Hg_2(SCN)_2^{2+}(aq)$ and also for $Hg_2Br_2^{2+}(aq)$ in solutions with high ionic strength.

XI. Other Inorganic Complexes and Compounds

For the hydride HgH(g) we adopt $S°$ = 52.50 cal K^{-1} mol^{-1} and $\Delta H_f°$ = 57 kcal mol^{-1} from spectroscopic data as discussed by Feber and Herrick[193] and also in the JANAF tables.[76] These values and the derived $\Delta G_f°$ 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

	K			
Reaction	NH_3	CH_3NH_2	$n\text{-}C_4H_9NH_2$	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	
$Hg^{2+}(aq) + 4L(aq) = HgL_4^{3+}(aq)$	2.0×10^{19}	3×10^{18}	1×10^{20}	

$$HgSeO_3(c) = Hg^{2+}(aq) + SeO_3^{2-}(aq) \quad K_{sp} = 1.4 \times 10^{-14}$$

$$Hg_2SeO_3(c) = Hg_2^{2+}(aq) + SeO_3^{2-}(aq) \quad K_{sp} = 6.0 \times 10^{-15}$$

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 Markovskii[194] for mercuric tellurite, $HgTeO_3$, 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 $\Delta G_f°$ values in Table I for these complexes are not much different from those listed earlier in NBS 270-4. The $\Delta H_f°$ values for the $Hg(NH_3)_n^{2+}(aq)$ complexes in NBS 270-4 are in good agreement with the calorimetric results of Yatsimirskii and Milyukov.[197] Earlier calorimetric results from Fyfe[198] 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 $Hg_2^{2+}(aq)$ that are stable enough to exist at reasonable concentrations in solution. Some examples are various phosphate complexes that we now consider.

Yamane and Davidson[199] and Watters and Simonaitis[200] have reported a considerable number of stability constants as summarized below (some are average values):

$$Hg_2^{2+}(aq) + P_2O_7^{4-}(aq) = Hg_2(P_2O_7)^{2-}(aq) \quad K = 3 \times 10^9$$

$$Hg_2^{2+}(aq) + 2P_2O_7^{4-}(aq) = Hg_2(P_2O_7)_2^{6-}(aq) \quad K = 10^2$$

$$Hg_2^{2+}(aq) + P_2O_7^{4-}(aq) + OH^-(aq) = Hg_2(P_2O_7)(OH)^{3-}(aq) \quad K = 5 \times 10^{15}$$

$$Hg_2^{2+}(aq) + P_2O_7^{4-}(aq) + 2OH^-(aq) = Hg_2(P_2O_7)(OH)_2^{4-}(aq) \quad K = 2 \times 10^{20}$$

Various other equilibrium constants for complexes of $Hg_2^{2+}(aq)$ with $P_3O_{10}^{5-}(aq)$ and $P_4O_{13}^{6-}$ have also been reported.[199,200] We list $\Delta G_f°$ values for the pyrophosphate complexes, but are unable to do the same for the other species because we have no $\Delta G_f°$ values for the aqueous polyphosphate ions.

From the work of Tummavouri[201] we take

$$Hg^{2+}(aq) + 4NO_2^-(aq) = Hg(NO_2)_4^{2-}(aq) \quad K = 1 \times 10^{11}$$

and calculate the corresponding $\Delta G_f°$ of $Hg(NO_2)_4^{2-}(aq)$.

Davis and Irish[202] have reviewed work on the association of $Hg^{2+}(aq)$ with $NO_3^-(aq)$ 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 $HgNO_3^+(aq)$ and $Hg(NO_3)_2(aq)$. More recent Raman work[203] suggests a slightly larger K_1 and smaller K_2, consistent with our tabulated $\Delta G_f°$ values.

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

$$Hg^{2+}(aq) + N_3^-(aq) = Hg(N_3)^+(aq) \quad K = 5.6 \times 10^7$$

$$Hg(N_3)^+(aq) + N_3^-(aq) = Hg(N_3)_2(aq) \quad K = 3.1 \times 10^7$$

Sillen[141] has listed $K_{sp} = 7.1 \times 10^{-10}$, based on the work of Suzuki,[205] as the solubility product for mercurous azide, $Hg_2(N_3)_2(c)$. This value is in good agreement with $K_{sp} = 7.0 \times 10^{-10}$ listed in the *Chemical Abstracts*[205] summary of Suzuki's work, which is described in terms of HgN_3. On the other hand, the free energies listed in NBS 270-4 and 270-3 lead to $K_{sp} = 7.8 \times 10^{-19}$. Further, Gray and Waddington[206] have combined their properties for $N_3^-(aq)$ with Suzuki's results to obtain a $\Delta G_f°$ that is in turn consistent with the solubility product we have calculated from NBS free energies. Because it seems likely that Gray and Waddington[206] and the compilers of NBS 270-4 have "correctly" interpreted Suzuki's results in terms of $Hg_2(N_3)(c)$ and $Hg_2^{2+}(aq)$, we adopt $K_{sp} = 7.8 \times 10^{-19}$ for mercurous azide, along with the corresponding $\Delta G_f°$. We also adopt the following potential:

$$Hg_2(N_3)_2(c) + 2e^- = 2Hg(liq) + 2N_3^-(aq) \quad E° = 0.260 \text{ V}$$

Calorimetric measurements by Gray and Waddington[206] have led to $\Delta H° = -29.87$ kcal mol^{-1} for precipitation of $Hg_2(N_3)_2(c)$, in reasonable agreement with their interpretation of the temperature coefficient results of Suzuki.[205] We use this calorimetric $\Delta H°$ to calculate the $\Delta H_f°$ and combine with the $\Delta G_f°$ to obtain the $S°$ of $Hg_2(N_3)_2(c)$.

The thermodynamic properties listed in NBS 270-4 for mercurous carbonate are consistent with the emf results of Saegusa[207] and also the following potential and solubility product:

$$Hg_2CO_3(c) + 2e^- = 2Hg(liq) + CO_3^{2-}(aq) \quad E° = 0.309 \text{ V}$$

$$Hg_2CO_3(c) = Hg_2^{2+}(aq) + CO_3^{2-}(aq) \quad K_{sp} = 3.5 \times 10^{-17}$$

Polarographic measurements by Nyman and Salazar[208] have led to the following equilibrium constants:

$$Hg^{2+}(aq) + 2S_2O_3^{2-}(aq) = Hg(S_2O_3)_2^{2-}(aq) \quad K = 2 \times 10^{29}$$

$$Hg^{2+}(aq) + 3S_2O_3^{2-}(aq) = Hg(S_2O_3)_3^{4-}(aq) \quad K = 6 \times 10^{30}$$

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

Sillen[141] 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 $Hg_2(IO_3)_2(c)$. Sillen[141] has also listed log $K_{sp} = -8.70$ for mercurous chromate and log $K_{sp} = -16.96$ (18°C) for mercurous tungstate. We combine these values with the $Hg_2^{2+}|Hg$ potential to calculate the following potentials:

$$Hg_2CrO_4(c) + 2e^- = 2Hg(liq) + CrO_4^{2-}(aq) \quad E° = 0.54 \text{ V}$$

$$Hg_2WO_4(c) + 2e^- = 2Hg(liq) + WO_4^{2-}(aq) \quad E° = 0.3_0 \text{ V}$$

Using the free energy of $CrO_4^{2-}(aq)$ from NBS 270-4, we also calculate the $\Delta G_f°$ of $Hg_2CrO_4(c)$ as in Table I.

Sillen[141] has quoted (from Toropova) the following:

$$Hg^{2+}(aq) + 4SeCN^-(aq) = Hg(SeCN)_4^{2-}(aq) \quad K = 8.9 \times 10^{29}$$

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

Bernard and Busnot[209] have reported $\Delta H_f{}^\circ = 66$ kcal mol^{-1} for mercuric cyanamide, $HgCN_2(c)$, on the basis of their calorimetric measurements.

The NBS 270-4 lists $\Delta H_f{}^\circ$ values for a considerable number of inorganic compounds of mercury, such as $HgX_2 \cdot nNH_3(c)$, etc. Because the original experimental results for these compounds have been cited[54,210] and discussed[54] earlier, we omit these compounds from our discussion and also from our Table I.

XII. Compounds and Complexes Containing Organic Components

Cox and Pilcher[10] have provided an excellent review of the thermochemical properties of a number of organomercury compounds. The $\Delta H_f{}^\circ$ values listed by Cox and Pilcher[10] 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 Wilmshurst[211] and to the investigation of redistribution equilibria of organomercury compounds by Reynolds and Daniel.[212]

Combination of $\Delta G_f{}^\circ$ values for mercurous acetate and aqueous acetate ion as listed in NBS 270-4 and NBS 270-3 leads to $E^\circ = 0.5047$ V for the $Hg_2(Ac)_2|Hg$ couple. Although Gryzin[213] has reported $E^\circ = 0.4982$ V for this couple, a value more positive than 0.5047 V seems better. Larson[214] has reported $E^\circ = 0.5116$ V, but Covington, Talukdar, and Thirsk[215] have recalculated to obtain $E^\circ = 0.5109$ and 0.5111 V, and have also reported $E^\circ = 0.5113$ V based on their own measurements. Most recently, Chen and Pan[216] have found $E^\circ = 0.5117$ V. We therefore adopt the following:

$$Hg_2Ac_2(c) + 2e^- = Hg(liq) + 2Ac^-(aq) \quad E^\circ = 0.5114 \text{ V}$$

$$Hg_2Ac_2(c) = Hg_2{}^{2+}(aq) + 2Ac^-(aq) \quad K_{sp} = 2.4 \times 10^{-10}$$

The dE°/dT results of Chen and Pan[216] lead to $S^\circ = 71$ cal K^{-1} mol^{-1} and $\Delta H_f{}^\circ = -201.4$ kcal mol^{-1} for $Hg_2Ac_2(c)$. Similar results from Larson[214] (his reported calculations are mistaken) and Gryzin[213] lead to larger entropies and less exothermic $\Delta H_f{}^\circ$ values. On the basis of these values and old calorimetric results (difficult to interpret) cited by Bichowsky and Rossini,[54] we adopt $S^\circ \simeq 74$ cal K^{-1} mol^{-1} and $\Delta H_f{}^\circ = -201$ kcal mol^{-1} for $Hg_2Ac_2(c)$. A third law entropy would be useful.

Basu and Aditya[217] have investigated the $Hg_2Ac_2|Hg$ 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 $HgAc^-(aq)$ from the ions. Martell[141] has listed $\beta_2 = 2.7 \times 10^8$ for formation of $HgAc_2(aq)$ 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 Banerjea 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 Srinivasan[220] have made measurements with sodium-responsive glass electrodes in cells without liquid junction and obtained the following standard potential for mercurous picrate:

$$Hg_2Pc_2(c) + 2e^- = 2Hg(liq) + 2Pc^-(aq) \quad E^\circ = 0.4924 \text{ V}$$

Combination of this potential with that for the $Hg_2{}^{2+}|Hg$ couple leads to $K_{sp} = 5.4 \times 10^{-11}$ for mercurous picrate, $Hg_2Pc_2(c)$. This value is in good agreement with $K_{sp} = 4.9 \times 10^{-11}$ from solubility measurements.[220] The emf method used by Covington and Srinivasan[220] should have useful applications to other systems.

Bertram and Bone[221] have measured the mercurous benzoate potential from 25 to 40°C and have reported for 25° the following:

$$Hg_2Bz_2(c) + 2e^- = 2Hg(liq) + 2Bz^-(aq) \quad E^\circ = 0.4263 \text{ V}$$

This potential corresponds to $K_{sp} = 3.2 \times 10^{-13}$ for $Hg_2Bz_2(c)$. The ΔH° and ΔS° values reported by Bertram and Bone[221] have been calculated incorrectly; correct values are $\Delta H^\circ = -29.3$ kcal mol^{-1} and $\Delta S^\circ = -32.3$ cal K^{-1} 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 $Hg_2C_2O_4|Hg$ couple and to $K_{sp} = 1.7 \times 10^{-13}$ for $Hg_2C_2O_4(c)$. This value is in good agreement with the value quoted by Latimer,[222] based on Brodsky's calculations with results of earlier measurements.

The $\Delta G_f{}^\circ$ listed in NBS 270-4 for $Hg(C_2O_4)_2{}^{2-}$ should (we believe) refer to the mercur*ous* complex, $Hg_2(C_2O_4)_2{}^{2-}(aq)$. Using the NBS 270-4 value for this free energy with that for aqueous oxalate ion, we calculate the following:

$$Hg_2{}^{2+}(aq) + 2C_2O_4{}^{2-}(aq) = Hg_2(C_2O_4)_2{}^{2-}(aq) \quad K = 9.2 \times 10^6$$

NBS free energies also lead to another equilibrium constant:

$$Hg_2{}^{2+}(aq) + C_2O_4{}^{2-}(aq) + OH^-(aq) = Hg(C_2O_4)(OH)^-(aq) \quad K = 1.1 \times 10^{13}$$

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

Equilibrium constants for formation of Hg(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]

$$HgCl_2(aq) + ma(aq) = HgCl(ma)^+(aq) + Cl^-(aq) \quad K = 2.5 \times 10^2$$

$$HgCl(ma)^+(aq) + ma(aq) = Hg(ma)_2{}^{2+}(aq) + Cl^-(aq) \quad K = 1.6 \times 10^2$$

The $\Delta G_f{}^\circ$ values listed in Table I are consistent with the equilibrium constants above and those in Table II. Our adopted $\Delta H_f{}^\circ$ and S° values are based on the calorimetric results of Partridge, Christensen, and Izatt.[223]

"Best" formation constants for Hg(II)–ethylenediamine complexes, based on the investigations of Watters and Mason[224] 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]

$$HgCl_2(aq) + en(aq) = HgCl(en)^+(aq) + Cl^-(aq) \quad K = 3.5 \times 10^5$$

$$HgCl(en)^+(aq) + en(aq) = Hg(en)_2{}^{2+}(aq) + Cl^-(aq) \quad K = 1.5 \times 10^4$$

Combination of these latter values with formation constants for $HgCl^+(aq)$ and $HgCl_2(aq)$ from Table II leads to $K = 0.8 \times 10^{23}$ for

$$Hg^{2+}(aq) + 2en(aq) = Hg(en)_2{}^{2+}(aq) \qquad (14)$$

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 Nyman[225] have calculated $\Delta H^\circ =$

-32.9 kcal mol^{-1} (from d ln K/dT) for the reaction represented by eq 14. Partridge, Christensen, and Izatt[223] have made calorimetric measurements leading to $\Delta H^\circ = -17.7$ kcal mol^{-1} for replacement of both Cl^- in $HgCl_2(aq)$ to yield $Hg(en)_2{}^{2+}(aq)$, which we combine with $\Delta H_f{}^\circ$ values already cited to obtain $\Delta H^\circ = -30.4$ kcal mol^{-1} for reaction 14. The 2.5 kcal mol^{-1} difference between these two ΔH° values is not unreasonably large in view of the difference in paths and the uncertainty in $\Delta H_f{}^\circ$ of $HgCl_2(aq)$ that has been discussed previously. We have weighted the calorimetric results most heavily in obtaining our tabulated $\Delta H_f{}^\circ$ values.

Watters and Mason[224] have also reported equilibrium constants for such species as $Hg(en)(OH)^+(aq)$, $Hg(en)_2H^{3+}(aq)$, etc.

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

$$Hg^{2+}(aq) + gl^-(aq) = Hg(gl)^+(aq) \quad K = 2 \times 10^{10}$$

$$Hg(gl)^+(aq) + gl^-(aq) = Hg(gl)_2(aq) \quad K = 9 \times 10^8$$

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]

$$HgCl_2(aq) + gl^-(aq) = HgCl(gl)(aq) + Cl^-(aq) \quad K = 2.6 \times 10^3$$

$$HgCl(gl)(aq) + gl^-(aq) + Hg(gl)_2{}^-(aq) + Cl^-(aq) \quad K = 4.1 \times 10^2$$

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

$$Hg^{2+}(aq) + 2gl^-(aq) = Hg(gl)_2(aq)$$

compared to 1.8×10^{19} from the product of the stepwise constants given above. The $\Delta H_f{}^\circ$ values listed in NBS 270-4 for $HgCl(gl)(aq)$ and $Hg(gl)_2(aq)$ 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 Hg(II)–EDTA complex, but some of these investigations illustrate a common problem in coordination chemistry, as follows. Calorimetric measurements by three sets of investigators[226-228] have led to $\Delta H = -18.9$, -19.2, and -18.9 kcal mol^{-1} for complex formation, while application of d ln K/dT to K values at different temperatures has led Moeller and Chu[229] to $\Delta H^\circ = -9.3$ kcal mol^{-1} for this same reaction. This discrepancy of ~10 kcal mol^{-1}, which is probably due to error in the latter work,[229] corresponds to a discrepancy of ~30 cal K^{-1} mol^{-1} in the entropy and is more than enough to invalidate molecular interpretations.

Carson, Laye, and Steele[230] have carried out calorimetric investigations of complexing of $Hg^{2+}(aq)$ by *trans*-1,2-diaminocyclohexanetetraacetic acid (CDTA) and have compared their $\Delta H = -16.05$ kcal mol^{-1} with -16.60 and -18.9 kcal mol^{-1} from earlier calorimetric investigations. We also note that two applications[231] of d ln K/dT have led to $\Delta H^\circ = -14.1$ and -13.7 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 Mortimer[232] 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 Campbell[233] have made electrochemical and calorimetric measurements on complexes of $Hg^{2+}(aq)$ with urea, semicarbazide, and sulfur and selenium analogs of these compounds. Ashurst, Finkelstein, and Rice[234] have carried out extensive investigations of cyanide–xanthate mixed complexes of $Hg^{2+}(aq)$ and have reported 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 $(CH_3)Hg^+(aq)$ with various ligands.[235] Some representative values follow:

$$(CH_3)Hg^+(aq) + OH^-(aq) = (CH_3)HgOH(aq) \quad K = 10^9$$

$$(CH_3)Hg^+(aq) + Cl^-(aq) = (CH_3)HgCl(aq) \quad K = 10^5$$

$$(CH_3)Hg^+(aq) + I^-(aq) = (CH_3)HgI(aq) \quad K = 10^8$$

$$(CH_3)Hg^+(aq) + CN^-(aq) = (CH_3)Hg(CN)(aq) \quad K = 10^{13}$$

Equilibrium constants for similar reactions with other ligands and also for reactions of various ligands with $(CH_3CH_2)Hg^+(aq)$ have been reported[235] along with solubility products for PhHgX and $(CH_3)HgX$ (Ph = phenyl and X = halide). Enthalpy and entropy changes are available for some of these reactions. We also have ionization constants[236] for fluoroalkylmercuric hydroxide and halides.

Smith and Bertrand[237] have measured solubilities of dimethylmercury in water and various salt solutions.

Mansy, Wood, Sprowles, and Tobias[238] have recently reported results of their investigation (by Raman spectroscopy) of binding of $(CH_3)Hg^+$ to pyrimidine nucleosides and nucleotides, and have also provided numerous references to related work involving mercury and/or important biomolecules.

Barnes[239] has reported enthalpies of decomposition of mercuric halide–dioxane complexes and has discussed the results in relation to structures of these compounds.

Farhangi and Graddon[240] have reported thermodynamic data for reactions of HgX_2 compounds with various Lewis bases in benzene solution.

Brusset and Madaule-Aubry[241] have reported thermodynamic data for $HgCl_2 \cdot 2CH_3OH(c)$. We do not know the source of the properties for $HgCl_2 \cdot CH_3OH(c)$ 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 Hg(liq) at several temperatures, with results leading to a $\Delta H_f{}^\circ$ for Hg(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.

Onat[243] has reported solubilities of Hg(liq) in water from 25 to 80°C. The results do not resolve the uncertainties in thermodynamic properties of Hg(aq) that were discussed in section III.

Case and Bignold[244] and Johansson et al.[245] have investigated the HgO|Hg electrode over wide ranges of temperature and found that it is a useful reference electrode for alkaline solutions at high temperatures.

Ammlung and Brill[246] have investigated "HgBrI" in the solid state and found that it is a homogeneous equilibrium mixture of $HgBr_2$, HgBrI, and HgI_2.

Distribution measurements by Nikolic and Gal[247] have led to K values (55–85°C) for mercuric chloride and bromide complexes in the melt of $NH_4NO_3 \cdot 2H_2O$.

Munir et al.[248] have investigated the sublimation of HgS(c,black) with results suggesting that the $\Delta H_f{}^\circ$ is less negative than the values we (-12.0 kcal mol^{-1}) and NBS 270-4 (-12.8 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:

$$Hg_2(HCOO)_2(c) + 2e^- = 2Hg(liq) + 2HCOO^-(aq) \quad E^\circ = 0.566_4\ V$$

This potential corresponds to $\Delta G_f° = -141.7$ kcal mol^{-1} for $Hg_2(HCOO)_2(c)$. Their $dE°/dT$ (10-30°C) leads to $\Delta H_f° = -180$ kcal mol^{-1} and $S° = 41$ cal K^{-1} mol^{-1} for $Hg_2(HCOO)_2(c)$.

Sundberg and Martin[250] 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 Henneike[251] have investigated the interaction of pyridine and 2,2′-bypyridyl 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 $\Delta H°$ values.

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XIV. References and Notes

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