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RECEIVED for review June 2, 1966. Accepted September 16, 1966.

Entropies of the Aqueous Zn^{+2}, Cd^{+2}, Hg^{+2}, and Hg_2^{+2} Ions

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Thermochemical and equilibrium data in the literature were used to calculate partial molal entropies for the aqueous Zn^{+2}, Cd^{+2}, Hg^{+2}, and Hg_2^{+2} ions. Several paths were considered in calculating each entropy value. Average values are: $\overline{S}_2^\circ = -26.0 \pm 1.4, -18.9 \pm 1.8, -5.4 \pm 1.5$, and 18.8 ± 2.0 cal. deg.$^{-1}$ mole^{-1} for the aqueous Zn^{+2}, Cd^{+2}, Hg^{+2}, and Hg_2^{+2} ions, respectively. The value for the Cd^{+2} ion is slightly lower than previous literature values. Those for the other ions substantiate values in the literature. "Best" values were chosen for the entropies of the aqueous ions and were combined with free energy data to calculate $\Delta H_f^\circ = -36.6, -18.3, 41.3$, and 40.1 kcal. mole^{-1} for the aqueous Zn^{+2}, Cd^{+2}, Hg^{+2}, and Hg_2^{+2} ions, respectively.

FOR a forthcoming review (*6*) of the thermodynamics and thermochemistry of the transition metal ions and their compounds we have reviewed literature data for the aqueous Zn^{+2}, Cd^{+2}, Hg_2^{+2}, and Hg^{+2} ions. Accurate heats and free energies of formation, and partial molal entropies for these species are necessary if the many solution equilibria and thermochemical studies, extant in the literature, are to be useful in calculating the thermodynamic properties for compounds and aqueous species involving these ions.

The partial molal entropies are of particular interest, since many such compounds, particularly of Zn^{+2} and Cd^{+2}, crystallize from their saturated solutions as hydrates—e.g., $CdBr_2 \cdot 4H_2O$ (c). "Third-law" entropies, based on low-temperature calorimetric studies, have been determined for only a few such hydrates (*12*), and the remaining entropies must be derived by "second-law" methods or be estimated. Of the estimation procedures available, that of Latimer (*14*) is deservedly popular and produces entropies that are generally within 2 to 3 cal. deg.$^{-1}$ mole^{-1} of experimental values. In compiling data tables for many compounds of a single element, there is no way of determining the internal consistency of such estimated entropies. "Second-law" entropies, based on a common partial molal entropy, have a built-in consistency, and are perhaps more useful for such tabulations. An example of such a "second-law" determination is indicated below for $ZnSO_4 \cdot 7H_2O$ (c).

Stephenson (*29*) has reviewed literature equilibrium and thermochemical data, and concludes that $\Delta S_1^\circ = 2.3$ cal. deg.$^{-1}$ mole^{-1}.

$$ZnSO_4 \cdot 7H_2O = Zn^{+2} + SO_4^{-2} + 7H_2O \qquad (1)$$

This datum, the partial molal entropies of Zn^{+2} and SO_4^{-2} ions (*12*) and the entropy of H_2O permit a calculation of $S^\circ = 93.4$ cal. deg.$^{-1}$ mole^{-1} for the heptahydrate. The "third-law" value (*12*) is 92.9 cal. deg.$^{-1}$ mole^{-1}.

Partial molal entropies are generally derived by one of two methods. The first is to derive an entropy increment from equilibrium and thermochemical data at a single temperature, $\Delta S_T^\circ = (\Delta H_T^\circ - \Delta G_T^\circ)/T$, and then a partial molal entropy (or more properly the sum of two partial molal entropies) by reversal of the procedure used for $ZnSO_4 \cdot 7H_2O$. The second method depends on evaluating an entropy increment from the temperature dependence of equilibrium data alone. This is most often achieved from e.m.f. studies, at several temperatures, for a cell reacting, in the case of Zn^{+2}, as $Zn + 2H^+ = Zn^{+2} + H_2$. The entropy increment, $\Delta S^\circ = nF\ (dE^\circ/dT)$, the entropies of Zn and H_2, and that of H^+ (assigned as zero by convention) suffice to determine the partial molal entropy of Zn^{+2} ion.

For systems where a thermodynamically reversible electrode can be prepared and used over a temperature interval large enough to determine dE°/dT precisely (*13*), the resultant entropy increment is as good as, or better than, one determined from equilibrium and thermal data. [King (*13*) discusses the precision required to obtain reliable temperature coefficients from equilibrium data.] For many systems, however, such electrodes are difficult to prepare and/or use, and the resultant entropy increments are either of poor precision or meaningless in terms of the assumed electrode reactions.

ENTROPY OF Zn^{+2} (aq)

Kelley and King (*12*) tabulate $\overline{S}^\circ_{Zn^{+2}} = -25.8$ cal. deg.$^{-1}$ mole^{-1} based on a value of -25.7 cal. deg.$^{-1}$ mole^{-1} derived by Latimer, Pitzer, and Smith (*15*) from data for $Zn + 2H^+ = Zn^{+2} + H_2$; and on a value of -25.9 cal. deg.$^{-1}$ mole^{-1} determined by Bates (*2*) from e.m.f. studies involving Zn electrodes. Singh (*27*) has repeated such e.m.f. measurements, and reports $\overline{S}^\circ_{Zn^{+2}} = -25.8834$ (!) cal. deg.$^{-1}$ mole^{-1}. The calculation involving the dissolution of $ZnSO_4 \cdot 7H_2O$ (Equation 1) may be reversed to give $\overline{S}^\circ_{Zn^{+2}} = -26.3$ cal. deg.$^{-1}$ mole^{-1}. Stephenson (*29*) also has reviewed data leading to $\Delta G^\circ_2 = -2.31$ kcal. mole^{-1}.

$$ZnSO_4 \cdot 6H_2O + H_2O(g) = ZnSO_4 \cdot 7H_2O \qquad (2)$$

Thomsen (*30*) and Barieau and Giauque (*1*) have determined the heats of solution of both the hexa- and heptahydrates, leading to $\Delta H^\circ_3 = -3.44$ kcal. mole^{-1}.

$$ZnSO_4 \cdot 6H_2O + H_2O(liq) = ZnSO_4 \cdot 7H_2O \qquad (3)$$

These values, data for H_2O (liq and g) (*14*) and ΔS°_1 give $\Delta S^\circ_4 = -9.2$ cal. deg.$^{-1}$ mole^{-1} for the dissolution of the hexahydrate,

$$ZnSO_4 \cdot 6H_2O = Zn^{+2} + SO_4^{-2} + 6H_2O \qquad (4)$$

From entropies (*12*) for the other species involved, we calculate $\overline{S}^\circ_{Zn^{+2}} = -27.0$ cal. deg.$^{-1}$ mole^{-1}.

The solubility (*28*), a slight extrapolation of activity coefficient data (*19*), and the vapor pressure of water over the saturated solution (*9*), combine to give $\Delta G^\circ_5 = -7.15$ kcal. mole^{-1}.

$$ZnBr_2 \cdot 2H_2O = Zn^{+2} + 2Br^- + 2H_2O \qquad (5)$$

The dissociation pressure of the dihydrate (*9*) data for H_2O (liq and g) (*14*) and ΔG°_5 lead to $\Delta G^\circ_6 = -10.24$ kcal. mole^{-1}.

$$ZnBr_2 = Zn^{+2} + 2Br^- \qquad (6)$$

Thomsen (*30*) and Paoletti (*17*) report heats of solution for the bromide. We have adopted the latter result, $\Delta H^\circ_6 = -16.65$ kcal. mole^{-1}, and calculate $\Delta S^\circ_6 = -21.5$ cal. deg.$^{-1}$ mole^{-1}. This value, and the entropies (*12*) of $ZnBr_2$ and Br^-, lead to $\overline{S}^\circ_{Zn^{+2}} = -28.4$ cal. deg.$^{-1}$ mole^{-1}.

The solubility (*28*), mean activity coefficient (*19*), and heat of solution (*3*) of ZnI_2 lead to $\Delta S^\circ_7 = -6.3$ cal. deg.$^{-1}$ mole^{-1}.

$$ZnI_2 = Zn^{+2} + 2I^- \qquad (7)$$

The entropy of the solid has been estimated (*12*) as 35.0 cal. deg.$^{-1}$ mole^{-1}, leading to $\overline{S}^\circ_{Zn^{+2}} = -24.5$ cal. deg.$^{-1}$ mole^{-1}.

Shchukarev, Lilich, and Latysheva (*23*) have determined the heat of solution of ZnO in acid. Their data extrapolate to $\Delta H^\circ_8 = -21.2$ kcal. mole^{-1}. From the solubility product of the oxide (*21*) and the ionization constant of water (*14*) we calculate $\Delta S^\circ_8 = -18.1$ cal. deg.$^{-1}$ mole^{-1} and $\overline{S}^\circ_{Zn^{+2}} = -24.4$ cal. deg.$^{-1}$ mole^{-1}.

$$ZnO + 2H^+ = Zn^{+2} + H_2O \qquad (8)$$

These results are summarized in Table I.

Table I. Entropy of Zn^{+2}(aq)

(ΔS°_{298} and $\overline{S}^\circ_{Zn^{+2}}$ in cal. deg.$^{-1}$ mole^{-1})

Reaction	ΔS°_{298}	$\overline{S}^\circ_{Zn^{+2}}$
$ZnSO_4 \cdot 7H_2O = Zn^{+2} + SO_4^{-2} + 7H_2O$	2.3	−26.3
$ZnSO_4 \cdot 6H_2O = Zn^{+2} + SO_4^{-2} + 6H_2O$	−9.4	−27.0
$ZnBr_2 = Zn^{+2} + 2Br^-$	−21.5	−28.4
$ZnI_2 = Zn^{+2} + 2I^-$	−6.3	−24.5
$ZnO + 2H^+ = Zn^{+2} + H_2O$	−18.1	−24.4
Av.		−26.0 ± 1.4
Latimer, Pitzer, and Smith (*15*)		−25.7 ± 1.0
Bates (*2*)		−25.9 ± 0.5
Value adopted		−25.9 ± 0.8

THE ENTROPY OF Cd^{+2} (aq)

Kelley and King (*12*) tabulate $\overline{S}^\circ_{Zn^{+2}} = -15.6$ cal. deg.$^{-1}$ mole^{-1}, that value being a mean of $\overline{S}^\circ_{Cd^{+2}} = -16.4$ cal. deg.$^{-1}$ mole^{-1} calculated by Latimer, Pitzer, and Smith (*15*) from the heat of solution of Cd in HCl (aq) (*3*), and of $\overline{S}^\circ_{Cd^{+2}} = -14.8$ cal. deg.$^{-1}$ mole^{-1} determined by Bates (*2*) from the e.m.f. of the Cd/Cd^{+2} electrode. Unlike Zn(II) solutions, those of Cd(II) generally contain the metal ion in one or more aqueous complexes. Extrapolation of the heat of solution in HCl (aq) to zero ionic strength is made difficult by the stability of $CdCl_n^{2-n}$ complexes. A 0.01*m* solution of $CdCl_2$ contains more than 50% of the Cd(II) as $CdCl^+$ (aq). Bates' e.m.f. measurements (*2*) involved a Cd electrode in the form of a two-phase amalgam. The partial molal free energy and entropy of Cd in this amalgam had to be determined in separate experiments. We have the following thermochemical paths to the entropy of the Cd^{+2} ion.

The hydrate in equilibrium with a saturated solution of cadmium sulfate is $CdSO_4 \cdot 8/3\ H_2O$. From the solubility (*28*), mean activity coefficient (*19*), and the activity of water in the saturated solution (*19*) we calculate $\Delta G^\circ_9 = 2.55$ kcal. mole^{-1}.

$$CdSO_4 \cdot 8/3\ H_2O = Cd^{+2} + SO_4^{-2} + 8/3\ H_2O \qquad (9)$$

Papadopoulos and Giauque (*18*) have determined the heat of solution (in 400 moles of H_2O). Using heat of dilution values (*20*) we calculate $\Delta H^\circ_9 = -4.36$ kcal. mole^{-1} and $\Delta S^\circ_9 = -23.2$ cal. deg.$^{-1}$ mole^{-1}. From the entropy of the hydrate (*12*) we find $\overline{S}^\circ_{Cd^{+2}} = -17.3$ cal. deg.$^{-1}$ mole^{-1}.

Anhydrous CdI_2 exists in equilibrium with its saturated solution. For its dissolution we have solubility (*28*) and activity (*19*) data leading to $\Delta G^\circ_{10} = 4.70$ kcal. mole^{-1}.

$$CdI_2 = Cd^{+2} + 2I^- \qquad (10)$$

Solutions of CdI_2 contain most of the Cd(II) as CdI^+, and the standard enthalpy of solution, ΔH°_{10}, contains a large contribution from the heat of dilution. Whether we extrapolate the heat of solution (*3*) using dilution data (*20*) or enthalpy data for the dissociation of the ion pair (*26*), the result is $\Delta H^\circ_{10} = 3.20$ kcal. mole^{-1}, and $\Delta S^\circ_{10} = -5.0$ cal. deg.$^{-1}$ mole^{-1}. The entropy of CdI_2 has been taken as 38.3 cal. deg.$^{-1}$ mole^{-1}—the mean of several determinations (*10, 12*)—leading to $\overline{S}^\circ_{Cd^{+2}} = -19.9$ cal. deg.$^{-1}$ mole^{-1}.

The heat of solution of CdO in $HClO_4$(aq) [which does not complex with Cd(II)] (*11*) has been determined (*25*) as $\Delta H^\circ_{11} = -26.2$ kcal. mole^{-1}.

$$CdO + 2H^+ = Cd^{+2} + H_2O \qquad (11)$$

Mah (*16*) has reported a calorimetric $\Delta H^\circ_f = -61.2$ kcal. mole^{-1} for CdO, leading to $\Delta H^\circ_f = -19.1$ kcal. mole^{-1} for the Cd^{+2} ion. From electrode potential measurements, Latimer calculates (*14*) $\Delta G^\circ_f = -18.6$ kcal. mole^{-1}, leading to $\overline{S}^\circ_{\mathrm{Cd}^{+2}} = -20.5$ cal. deg.$^{-1}$ mole^{-1}.

The hydrate precipitated from a saturated solution of cadmium chloride is $CdCl_2 \cdot 5/2\ H_2O$. Its solubility (*28*) and activity and osmotic coefficients (*19*) lead to $\Delta G^\circ_{12} = 2.64$ kcal. mole^{-1}. Thomsen's heat of solution (*30*) and dilution data (*20*) lead to $\Delta H^\circ_{12} = -1.87$ kcal. mole^{-1}, and with the free energy to

$$CdCl_2 \cdot 5/2\ H_2O = Cd^{+2} + 2Cl^- + 5/2\ H_2O \qquad (12)$$

$\Delta S^\circ_{12} = -2.6$ cal. deg.$^{-1}$ mole^{-1}. The heats of solution (*3*) and dissociation pressures (*8*) of the hydrates $CdCl_2 \cdot nH_2O$ (n = 0,1, and 5/2) give $\Delta S^\circ_{13} = -85.5$ cal. deg.$^{-1}$ mole^{-1}. Assuming that

$$CdCl_2 + 5/2\ H_2O\ (g) = CdCl_2 \cdot 5/2\ H_2O \qquad (13)$$

the molar contribution of bound water in the chloride hydrates is the same as that in the sulfate hydrates (*12*), we calculate $\Delta S^\circ_{13} = -87.2$ cal. deg.$^{-1}$ mole^{-1}. Since the relative heats of solution and the dissociation pressures are not particularly precise, we average these values, and with the entropy (*10*) of $CdCl_2$, we calculate $\overline{S}^\circ_{\mathrm{Cd}^{+2}} = -18.2$ cal. deg.$^{-1}$ mole^{-1}. The results for Cd^{+2} ion are summarized in Table II.

ENTROPY OF Hg^{+2} (aq)

Rossini *et al.* (*20*) did not include entropy values for either Hg_2^{+2} or Hg^{+2} ions. Latimer, Pitzer, and Smith (*15*) report $\overline{S}^\circ_{\mathrm{Hg}_2^{+2}} = 17.7$ cal. deg.$^{-1}$ mole^{-1} from consideration of data for 2 Hg(liq) + $2H^+ = Hg_2^{+2} + H_2$. Latimer (*14*) tabulates 17.7 and −6.5 cal. deg.$^{-1}$ mole^{-1} for the entropies of Hg_2^{+2} and Hg^{+2}, respectively, in the first edition of "Oxidation Potentials," but only −5.4 cal. deg.$^{-1}$ mole^{-1} for Hg^{+2} in the second edition. The 1961 entropy compilation of Kelley and King (*12*) includes only the 17.7 cal. deg.$^{-1}$ mole^{-1} value for the Hg_2^{+2} ion.

Compounds of Hg(II) are largely covalent and while more soluble than those of Hg(I) are much less soluble than their Zn and Cd analogs. With the exception of salts of oxyanions, Hg(II) compounds are extremely weak electrolytes, and the change in state corresponding to the dissolution of a Hg(II) halide may be written as $HgX_2(c) = HgX_2(aq)$.

The solubility (*28*) of $HgCl_2$ is approximately 0.3m. We have assumed its activity coefficient to be unity, and calculate $\Delta G^\circ_{14} = 0.71$ kcal. mole^{-1}. Thomsen (*30*) reports a heat of solution, $\Delta H^\circ_{14} = 3.30$ kcal. mole^{-1}, leading to $\Delta S^\circ_{14} = 8.8$ cal. deg.$^{-1}$ mole^{-1}.

$$HgCl_2(c) = HgCl_2(aq) \qquad (14)$$

We combine this result with $\Delta S^\circ_{15} = -6.7$ and $\Delta S^\circ_{16} = -13.0$ cal. deg.$^{-1}$ mole^{-1} to obtain $\Delta S^\circ_{17} = -10.9$ cal. deg.$^{-1}$ mole^{-1}.

$$HgCl_2(aq) = HgCl^+ + Cl^- \qquad (15)$$

$$HgCl^+ = Hg^{+2} + Cl^- \qquad (16)$$

$$HgCl_2(c) = Hg^{+2} + 2Cl^- \qquad (17)$$

Table II. Entropy of Cd^{+2}(aq)

(ΔS°_{298} and $\overline{S}^\circ_{\mathrm{Cd}^{+2}}$ in cal. deg.$^{-1}$ mole^{-1})

Reaction	ΔS°_{298}	$\overline{S}^\circ_{\mathrm{Cd}^{+2}}$
$CdSO_4 \cdot 8/3\ H_2O = Cd^{+2} + SO_4^{-2} + 8/3 H_2O$	−23.2	−17.3
$CdI_2 = Cd^{+2} + 2I^-$	−5.0	−19.9
$CdO + 2H^+ = Cd^{+2} + H_2O$	−16.9	−20.5
$CdCl_2 \cdot 5/2\ H_2O = Cd^{+2} + 2Cl^- + 5/2 H_2O$	−2.6	−18.2
Av.		−18.9 ± 1.8
Latimer, Pitzer, and Smith (*15*)		−16.4 ± 1.5
Bates (2)		−14.8 ± 1.0
Value adopted		−18.0 ± 2.5

Using data (*12*) for $HgCl_2$ and Cl^-, we calculate $\overline{S}^\circ_{\mathrm{Hg}^{+2}} = -3.4$ cal. deg.$^{-1}$ mole^{-1}.

Values cited for the dissociation of Hg(II) complex ions are "best" values, the derivation of which is discussed by Hepler and Wulff (*6*). Most of the equilibrium data are given by Sillen and Martell (*26*).

The solubility (*28*) of $HgBr_2$ is close to 0.017m, leading to $\Delta G^\circ_{18} = 2.42$ kcal. mole^{-1}.

$$HgBr_2(c) = HgBr_2(aq) \qquad (18)$$

The low solubility of the bromide precludes accurate heat of solution measurements, but Bichowsky and Rossini (*3*) quote a value of $\Delta H^\circ_{18} = 2.4$ kcal. mole^{-1} determined by Berthelot. This leads to $\Delta S^\circ_{18} = -0.1$ cal. deg.$^{-1}$ mole^{-1}, and with values (*6, 26*) for $HgBr_2$(aq) and $HgBr^+$(aq) to $\Delta S^\circ_{19} = -8.8$ cal. deg.$^{-1}$ mole^{-1}.

$$HgBr_2(c) = Hg^{+2} + 2Br^- \qquad (19)$$

From the entropies (*12*) of $HgBr_2$(c) and Br^-, we then calculate $\overline{S}^\circ_{\mathrm{Hg}^{+2}} = -7.5$ cal. deg.$^{-1}$ mole^{-1}.

The iodide is only sparingly soluble (*28*), $m = 10^{-4}$, and heat of solution measurements cannot be made. From the solubility we calculate $\Delta G^\circ_{20} = 5.43$ kcal. mole^{-1}, and combine this result with values (*6, 26*) for HgI_2(aq) and HgI^+ to give $\Delta G^\circ_{21} = 38.1$ kcal. mole^{-1}.

$$HgI_2(c) = HgI_2(aq) \qquad (20)$$

Thomsen (*30*) determined the heat of solution of the iodide in excess I^- as $\Delta H^\circ_{22} = -3.48$ kcal. mole^{-1}.

$$HgI_2(c) = Hg^{+2} + 2I^- \qquad (21)$$

We combine this with our value (*6, 26*) for the heat of dissociation of HgI_4^{-2}, to yield $\Delta H^\circ_{21} = 39.6$ kcal. mole^{-1} and $\Delta S^\circ_{21} = 5.1$ cal. deg.$^{-1}$ mole^{-1}.

$$HgI_2 + 2I^- = HgI_4^{-2} \qquad (22)$$

For the Hg^{+2} ion we then calculate $\overline{S}^\circ_{\mathrm{Hg}^{+2}} = -5.7$ cal. deg.$^{-1}$ mole^{-1}.

Shchukarev *et al.* (*24*) have determined the heat of solution of HgO(red) in $HClO_4$(aq). We have extrapolated their results to $\Delta H^\circ_{23} = -5.6$ kcal. mole^{-1}. Feitknecht and Schindler (*4*) give the solubility product of the oxide as 4 × 10^{-26}, leading to $\Delta G^\circ_{23} = -4.0$ kcal. mole^{-1} and $\Delta S^\circ_{23} = -5.3$ cal. deg.$^{-1}$ mole^{-1}.

$$HgO(red) + 2H^+ = Hg^{+2} + H_2O \qquad (23)$$

Using 17.4 cal. deg.$^{-1}$ mole^{-1} for the entropy of HgO(red) (*5*) we calculate $\overline{S}^\circ_{\mathrm{Hg}^{+2}} = -4.9$ cal. deg.$^{-1}$ mole^{-1}.

ENTROPY OF Hg_2^{+2}(aq)

Schwartzenbach and Anderegg (*22*) have studied the electrode potential corresponding to Equation 24 as a function of temperature and report $\Delta S^\circ_{24} = 6.0$ cal. deg.$^{-1}$ mole^{-1}. Using our average value for $\overline{S}^\circ_{\mathrm{Hg}^{+2}}$, −5.4 cal. deg.$^{-1}$ mole^{-1}, we calculate $\overline{S}^\circ_{\mathrm{Hg}^{+2}} = 18.8$ cal. deg.$^{-1}$ mole^{-1}.

$$Hg(liq) + Hg^{+2} = Hg_2^{+2} \qquad (24)$$

The results for Hg^{+2} and Hg_2^{+2} ions are summarized in Table III.

THERMODYNAMIC PROPERTIES OF Zn^{+2}, Cd^{+2}, Hg_2^{+2}, and Hg^{+2} IONS

Of the values in Table I for $\overline{S}^\circ_{\mathrm{Zn}^{+2}}$ those based on the thermochemistry of the sulfate and oxide are probably the most reliable. We have weighted these heavily in computing the average $\overline{S}^\circ_{\mathrm{Zn}^{+2}} = -26.0 \pm 1.4$ cal. deg.$^{-1}$ mole^{-1}. This value is in good accord with those of Latimer, Pitzer, and Smith (*15*) and Bates (*2*). Latimer (*14*) gives 0.763 volt for the Zn/Zn^{+2} potential, leading to $\Delta G^\circ_f = -35.18 \pm 0.05$ kcal. mole^{-1}, and with $\overline{S}^\circ_{\mathrm{Zn}^{+2}} = -25.9 \pm 0.8$ cal. deg.$^{-1}$ mole^{-1}, to $\Delta H^\circ_f = -36.5_6 \pm 0.3_1$ kcal. mole^{-1}.

Table III. Entropies of Hg^{+2}(aq) and Hg_2^{+2}(aq)

(ΔS°_{298} and $\overline{S}^\circ_2$ in cal. deg.$^{-1}$ mole^{-1})

Reaction	ΔS°_{298}	$\overline{S}^\circ_{\mathrm{Hg}^{+2}}$
$HgCl_2 = Hg^{+2} + 2Cl^-$	−10.9	−3.4
$HgBr_2 = Hg^{-2} + 2Br^-$	−8.8	−7.5
$HgI_2 = Hg^{+2} + 2I^-$	5.1	−5.7
$HgO + 2H^- = Hg^{+2} + H_2O$	−5.4	−4.9
Av.		−5.4 ± 1.5
Latimer, 2nd ed. (*14*)		−5.4
Value adopted		−5.4 ± 1.5
		$\overline{S}^\circ_{\mathrm{Hg}_2^{+2}}$
$Hg_2^{+2} = Hg^{+2} + Hg(liq)$	−6.0	18.8 ± 2.0
Latimer, Pitzer, and Smith (*15*)		17.7 ± 3.0
Value adopted		18.3 ± 2.0

For Cd^{+2} ion the values based on the dissolution of the sulfate and iodide have been weighted more heavily in averaging to $\overline{S}^\circ_{\mathrm{Cd}^{+2}} = -18.9 \pm 1.8$ cal. deg.$^{-1}$ mole^{-1}. This value is more negative then those given by Latimer, Pitzer, and Smith (*15*) or Bates (*2*) but overlaps the former within the combined uncertainties. We adopt $\overline{S}^\circ_{\mathrm{Cd}^{+2}} = -18.0 \pm 2.5$ cal. deg.$^{-1}$ mole^{-1}. Latimer gives $E^\circ = 0.403$ volt for the Cd/Cd^{+2} potential, leading to $\Delta G^\circ_f = -18.59 \pm 0.08$ kcal. mole^{-1} and $\Delta H^\circ_f = 18.3_4 \pm 0.7_8$ kcal. mole^{-1} for Cd^{+2} ion.

The mean value for $\overline{S}^\circ_{\mathrm{Hg}^{+2}}$ is -5.4 ± 1.5 cal. deg.$^{-1}$ mole^{-1}, in accord with that given by Latimer (*14*). That derived for Hg_2^{+2}, 18.8 ± 2.0 cal. deg.$^{-1}$ mole^{-1}, is in agreement with the value determined by Latimer, Pitzer, and Smith (*15*). We adopt 18.3 ± 2.0 cal. deg.$^{-1}$ mole^{-1} for Hg_2^{+2}. Recent values for the $Hg(liq)/Hg_2^{+2}$ potential (*26*) center about $E^\circ = -0.791$ volt, leading to $\Delta G^\circ_f = 36.48 \pm 0.10$ kcal. mole^{-1}, and with the entropy adopted above, to $\Delta H^\circ_f = 40.08 \pm 0.7_5$ kcal. mole^{-1}, for the Hg_2^{+2} ion. Hietanen and Sillen (*7*) have reviewed data for the disproportionation of Hg_2^{+2} and give $K_{24} = 88 \pm 4$. From this result we calculate $\Delta G^\circ_f = 39.13 \pm 0.1_3$ kcal. mole^{-1} and $\Delta H^\circ_f = 41.25 \pm 0.6_4$ kcal. mole^{-1} for the Hg^{+2} ion.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The partial financial support of the National Aeronautics and Space Administration through Sustaining Grant NGR-46-001-008 to the University of Vermont (to CAW). The author thanks Loren G. Hepler for assistance and for the use of facilities at Carnegie Institute of Technology supported by the National Science Foundation.

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RECEIVED for review June 6, 1966. Accepted September 21, 1966. Division of Physical Chemistry, 151st meeting, ACS, Pittsburgh, Pa., March 1966.

Ideal Gas Thermodynamic Functions of Terbium, Erbium, Thulium, and Plutonium

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Improved ideal gas thermodynamic functions are calculated for monatomic terbium, erbium, thulium, and plutonium using recent energy level data. The functions are tabulated from 100° to 6000° K. at 100° intervals.

THE IDEAL GAS thermodynamic functions of monatomic terbium, erbium, thulium, and plutonium, which were previously calculated from 100° to 6000° K. at 100° intervals (*9*), are improved by recalculation with more extensive energy level data. The reference temperature is 298.15° K., and the gases are assumed to be ideal at 1 atm. pressure.

The number of levels, the range of energies of the levels, and the term designation of the lowest level are given for each element. All available experimentally established levels and some predicted levels are included in the computations. Continuing analyses of the complex spectra of these elements can be expected to establish additional levels