Entropies of Some Aqueous Transition Metal Ions

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Thermodynamic data have been used for new calculations of standard partial molal entropies of several transition metal ions in aqueous solution. Results of these calculations for Ni^{2+} (aq), Co^{2+} (aq), Fe^{2+} (aq), Cu^{2+} (aq) and Mn^{2+} (aq) are −29.5, −26.6, −26.2, −20.4 and −21 cal. mole^{-1} deg.$^{-1}$, respectively. These calculations and accompanying discussion illustrate the need for more heat of solution and low temperature heat capacity measurements on hydrated crystals.

DATA ARE available at present which permit new calculations of entropies of several transition metal ions.

Entropy of Ni^{2+} (aq.). Busey and Giauque (*2*) have calculated the standard heat of formation of $NiCl_2$(c) to be −72.974 cal. mole^{-1} at 298° K. NBS data (*9*) based upon experimental work of Thomsen, permit us to calculate that $\Delta H^\circ = -19.6$ kcal. mole^{-1} for solution of $NiCl_2$(c) in water. More recent experiments (*8*) gave $\Delta H^\circ = -19.7$ kcal. mole^{-1}. We shall take $\Delta H^\circ = -19.7$ kcal. mole^{-1} for our calculations. Combination of the heats of formation and solution of $NiCl_2$(c) with the heat of formation of Cl^-(aq) (*9*) leads to −12.7 kcal. mole^{-1} for the standard heat of formation of Ni^{2+}(aq). Carr and Bonilla (*3*) have determined E° = 0.232*v* for the Ni/Ni^{2+} couple, in good agreement with E° from Haring and Bosche (*5*). We calculate −11.5 kcal. mole^{-1} for the standard free energy of formation of Ni^{2+}(aq). Combination of this free energy of formation with the heat of formation of Ni^{+2}(aq) given above and entropies of Ni(c) (*1*) and H_2(g) (*9*) leads to −30.8 cal. deg.$^{-1}$ mole^{-1} for the standard partial molal entropy of Ni^{2+}(aq).

It is also possible to calculate the entropy of Ni^{2+}(aq) from data on $NiCl_2 \cdot 6H_2O$ (*14*). The reaction to be considered is

$$NiCl_2 \cdot 6H_2O\,(c) = NiCl_2(aq) + 6H_2O\,(liq) \qquad (1)$$

The standard free energy of solution of $NiCl_2 \cdot 6H_2O$(c) is calculated from

$$\Delta F_1^\circ = -RT \ln\,(4m^3\gamma_\pm^3 a_w^6) = -4260 \text{ cal. mole}^{-1} \qquad (2)$$

where m, $\gamma_\pm$, and a_w represent the molal solubility, the mean activity coefficient in saturated solution, and the activity of water in saturated solution. The solubility is given by Seidell (*13*). The mean activity coefficient is taken from Robinson and Stokes (*11*) and the activity of water is calculated from the appropriate osmotic coefficient also given by Robinson and Stokes.

NBS data (*9*), based on work of Thomsen, lead to ΔH_1° = 720 cal. mole^{-1}, from which ΔS_1° = 16.7 cal. deg.$^{-1}$ mole^{-1} is calculated. Friedberg (*4*) has recently given us his unpublished heat capacity data on $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ from which we have calculated 82.3 and 83.4 cal. deg.$^{-1}$ mole^{-1}, respectively, for the entropies at 298° K. Combination of this entropy of $NiCl_2 \cdot 6H_2O$ with entropies of Cl^-(aq) and H_2O(liq) (*9*) and ΔS_1° leads to −28.3 cal. deg.$^{-1}$ mole^{-1} for the standard partial molal entropy of Ni^{2+}(aq). Friedberg's measurements extended to 1° K. so that "magnetic entropy" is included in the entropy values given here.

This value for the entropy of Ni^{2+}(aq) differs considerably from that calculated by Stavely and Randall (*14*) because we have used a different value (82.3) for the entropy of $NiCl_2 \cdot 6H_2O$ than they did (87.8), which was based upon an estimate suggested by Walkley (*15*). The procedure developed by Latimer (*7*) for estimation of entropies yields 83.1 cal. deg.$^{-1}$ mole^{-1} for the entropy of $NiCl_2 \cdot 6H_2O$(c), which is in good agreement with the experimental value.

Values for the entropy of Ni^{2+}(aq) have also been calculated from data on $NiSO_4 \cdot 7H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ and their saturated solutions. Heats of solution have been calculated from NBS data (*9*). Activity coefficients and osmotic coefficients are from Robinson and Stokes (*11*) and solubilities are from Seidell (*13*). Following Latimer (*7*), the entropies of $NiSO_4 \cdot 7H_2O$(c) and $Ni(NO_3)_2 \cdot 6H_2O$(c) were estimated to be 93.5 and 102.3 cal. deg.$^{-1}$ mole^{-1}, respectively. The entropy for Ni^{2+}(aq) so obtained from $NiSO_4 \cdot 7H_2O$(c) is −29.9 cal. deg.$^{-1}$ mole^{-1} and the value obtained from $Ni(NO_3)_2 \cdot 6H_2O$(c) is −28.7 cal. deg.$^{-1}$ mole^{-1}.

By weighting the first two values for the entropy of Ni^{2+}(aq) more heavily than the last two, −29.5 cal. deg.$^{-1}$ mole^{-1} is taken as the best standard partial molal entropy of Ni^{2+}(aq).

Entropy of Co^{2+}(aq). The solubility (*13*), heat of solution (*9*), activity coefficient in saturated solution (*11*), and entropies of Cl(aq), H_2O(liq) (*9*) and $CoCl_2 \cdot 6H_2O$(c) (*4*) were used with the cobalt analogue of reaction (*1*) to calculate that the standard partial molal entropy of Co^{2+}(aq) is −22.8 cal. deg.$^{-1}$ mole^{-1}.

Stavely and Randall (*14*) have calculated $\Delta S^\circ = -1.4$ cal. deg.$^{-1}$ mole^{-1} for the reaction $Co^{2+}(aq) + Ni(c) = Ni^{2+}(aq) + Co(c)$. Combination of this ΔS° with the entropies of the metals and our best entropy for Ni^{2+}(aq) leads to −28.5 cal. deg.$^{-1}$ mole^{-1} for the entropy of Co^{2+}(aq). The above $\Delta S^\circ = -1.4$ cal. deg.$^{-1}$ mole^{-1} is partly based upon taking the potential for the Co/Co^{2+} couple to be 0.027*v* greater than the potential for the Ni/Ni^{2+} couple. Many values for the Co/Co^{2+} potential have been reported and what value is the best is not at all clear. Review of the literature suggests that the work of Haring and Westfall (*6*) leading to a potential of 0.278*v* is preferable to the value, 0.259*v*, obtained by adding 0.027*v* to the Ni/Ni^{2+} potential due to Carr and Bonilla (*3*). Using the potential 0.278*v* for Co/Co^{2+} (a difference of 0.046*v* between Co/Co^{2+} and Ni/Ni^{2+}) leads to −25.7 cal. deg.$^{-1}$ mole^{-1} for the entropy of Co^{2+}(aq).

The entropy of Co^{2+}(aq) can also be calculated from data on $CoCl_2$ and the above (*6*) Co/Co^{2+} potential. For the heat of formation of $CoCl_2$(c) we take −76.1 kcal. mole^{-1} as reported by Sano (*12*) and the heat of solution from the data of Thomsen as given in NBS Circular 500 (*9*). This calculation leads to −29.6 cal. deg.$^{-1}$ mole^{-1} for the entropy of Co^{2+}(aq).

We have estimated the entropies of $CoSo_4 \cdot 7H_2O$(c) and $CoBr_2 \cdot 6H_2O$(c) by Latimer's procedure (*7*) to be 93.6 and 88.8 cal. deg.$^{-1}$ mole^{-1}, respectively. These entropies, combined with other data for these compounds, lead to −26.3 and −26.0 cal. deg.$^{-1}$ mole^{-1} for the entropy of Co^{2+}(aq).

As the best value for the entropy of Co^{2+}(aq) we take the average of all the values we have calculated, which is −26.6 cal. deg.$^{-1}$ mole^{-1}. We can offer no explanation for the entropy derived from $CoCl_2 \cdot 6H_2O$ (c) being less negative than any of the others.

Entropy of Fe^{2+}(aq). NBS Circular 500 lists (*9*) −27.1 cal. deg.$^{-1}$ mole^{-1} for the entropy of Fe^{2+}(aq). This value is based upon thermal data that are not entirely consistent and 0.440*v* for the standard Fe/Fe^{2+} potential. Patrick and Thompson (*10*) have reinvestigated the Fe/Fe^{2+} potential and reported 0.409*v*. Combination of the free energy calculated from this latter potential with NBS data (*9*) leads to −31.7 cal. deg.$^{-1}$ mole^{-1} for the entropy of Fe^{2+}(aq). Using various combinations of the available heat and free energy data we have calculated values for the entropy of Fe^{2+}(aq) as negative as −33.1 and as large as −21.7 cal. deg.$^{-1}$ mole^{-1}. We estimate that about −27 cal. deg.$^{-1}$ mole^{-1} is the best entropy that can be obtained from these data.

We have estimated the entropies of $FeCl_2 \cdot 4H_2O$(c) and $FeSO_4 \cdot 7H_2O$(c) according to Latimer's procedure (*7*) to be 66.2 and 91.5 cal. deg.$^{-1}$ mole^{-1}, respectively. These data have been used in calculations like those already discussed for nickel and cobalt compounds to obtain −26.7 and −24.8 cal. deg.$^{-1}$ mole^{-1} for entropy of Fe^{2+}(aq).

Entropy of Cu^{2+}(aq). NBS (*9*) values for the heat of solution and entropy of $CuSO_4 \cdot 5H_2O$(c) have been combined with solubility (*13*) and activity (*11*) data to obtain −20.4 cal. deg.$^{-1}$ mole^{-1} for the entropy of Cu^{2+}(aq). Estimated entropies (*7*) of $CuCl_2 \cdot 2H_2O$(c) and $Cu(NO_3)_2 \cdot 6H_2O$(c) lead to −20.8 and −20.1 cal. deg.$^{-1}$ mole^{-1} for the entropy of Cu^{2+}(aq). NBS Circular 500 (*9*) lists −23.6 cal. deg.$^{-1}$ mole^{-1} for this entropy but larger and smaller values have appeared and been used from time to time.

Entropy of Mn^{2+}(aq). There is considerable uncertainty in the value of −20 cal. deg.$^{-1}$ mole^{-1} listed (*9*) for the entropy of Mn^{2+}(aq). We have estimated the entropies of $MnCl_2 \cdot 4H_2O$(c) and $MnSO_4 \cdot H_2O$(c) (*7*) and combined these values with solubility (*13*), heat of solution (*9*) and activity (*11*) data to calculate −20.5 and −21.1 cal. deg.$^{-1}$ mole^{-1} for the entropy of Mn^{2+}(aq).

DISCUSSION

Although high accuracy cannot be claimed for any of the entropies reported here, they are more reliable than most of the values reported elsewhere for these ions. Our calculations have served to emphasize that there are still large uncertainties in the thermodynamic properties of some of the most common and important ionic species and that more measurements of heat capacities of hydrated crystals leading to Third Law entropies are needed along with measurements of heats of solution. Because of difficulties associated with investigations of electrode behavior of such metals as iron, cobalt, nickel, and manganese, the most reliable values of thermodynamic properties of ions of these elements will ultimately be derived from thermal measurements.

Table I. Entropies of Aqueous Ions

Ion	$\bar{S}_2^\circ$ (cal./deg. mole)
Ni^{2+}(aq)	−29.5 ± 1.5
Co^{2+}(aq)	−26.6 ± 2.5
Fe^{2+}(aq)	−26.2 ± 3.0
Cu^{2+}(aq)	−20.4 ± 1.0
Mn^{2+}(aq)	−21 ± 3

Best values for the standard partial molal entropies discussed are given in Table I, along with our estimates of the uncertainty associated with each value.

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