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THE ENTHALPY OF SOLUTION OF FERROUS CHLORIDE IN WATER AT 298 K

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ABSTRACT

We have made calorimetric measurements of the enthalpy of dissolving solid ferrous chloride in water at 298 K and have derived $\Delta H^\circ = -19.82$ kcal mol^{-1} for the standard enthalpy of this process. This ΔH° is related by way of some thermodynamic calculations to other properties of iron.

INTRODUCTION

There are substantial uncertainties in the thermodynamic properties of Fe^{2+}(aq) and of various related ions and compounds of iron, as partly summarized below.

Long ago Latimer[1] selected $\Delta G_f^\circ = -20.31$ kcal mol^{-1} for

$$Fe^{2+}(aq) + 2e^- = Fe(c) \qquad (1)$$

from e.m.f. measurements of Randall and Frandsen[2] at 298 K. More recently, Patrick and Thompson[3] have reported $E^\circ = -0.409$ V for this same potential, which corresponds to $\Delta G_f^\circ = -18.86$ kcal mol^{-1} for Fe^{2+}(aq). Still more recently, Hurlen[4] has made e.m.f. measurements that led him to $E^\circ = -0.467$ V at 293 K. Combination of thermal data with the Gibbs-Helmholtz equation shows that $(dE^\circ/dT)(5^\circ)$ is 10^{-3} V or less so that we can take Hurlen's E° as also applying at 298 K and thence leading to $\Delta G_f^\circ = -21.5$ kcal mol^{-1} for Fe^{2+}(aq). Thus we see that results of careful measurements have led to spreads of 0.058 V in E° and 2.6 kcal mol^{-1} in ΔG_f° values.

The NBS Circ. 500[5] lists $\Delta G_f^\circ = -20.3$ kcal mol^{-1} for Fe^{2+}(aq), in accord with the E° from Randall and Frandsen[2]. This compilation[5] also gives $\Delta H_f^\circ = -21.0$ kcal mol^{-1} and $S^\circ = -27.1$ cal K^{-1} mol^{-1} for Fe^{2+}(aq). The more recent NBS Tech. Note 270-4[6] lists $\Delta G_f^\circ = -18.85$ kcal mol^{-1}, $\Delta H_f^\circ = -21.3$ kcal mol^{-1}, and $S^\circ = -32.9$ cal K^{-1} mol^{-1} for Fe^{2+}(aq), with this free energy in accord with the potential from Patrick and Thompson[3].

Larson et al.[7] have shown that a combination of calorimetric results with a standard free energy of solution for $FeSO_4 \cdot 7H_2O(c)$ leads to $\Delta G_f^\circ = -21.8$ kcal mol^{-1}, $\Delta H_f^\circ = -22.1$ kcal mol^{-1}, and $S^\circ = -25.6$ cal K^{-1} mol^{-1} for Fe^{2+}(aq).

This ΔG_f° corresponds to $E^\circ = -0.47_3$ V, which is in agreement with the potential from Hurlen[4] but not with potentials from earlier[2, 3] investigations.

As one part of a program intended to diminish discrepancies cited above (and others that involve various compounds of iron), we have investigated the enthalpy of solution of $FeCl_2$(c) with results that are reported here.

EXPERIMENTAL

Our preliminary experiments with ferrous chloride and previous experience with other MCl_2(c) compounds showed that the principal difficulty to be expected in this investigation would involve preparation and subsequent handling of dry $FeCl_2$(c). The procedures described below were developed and carried out in order to minimize these difficulties and their consequences.

Fisher Certified $FeCl_2 \cdot 4H_2O$(c) was placed in a glass tube that was then evacuated and heated slowly to 200°C over a period of about 1 h to remove part of the water of hydration. The resulting partly dehydrated material was transferred to a quartz tube and further dried by heating in a stream of dry HCl(g) at 550°C for 4 h. A small amount of $FeCl_3$(c) that condensed in the cold end of the tube was removed and the remaining $FeCl_2$(c) was again heated in a stream of dry HCl(g) at 550°C for 4 h. The tube containing the dry $FeCl_2$(c) was transferred to a dry box in which we maintained a dry and oxygen-free atmosphere. Samples for analysis were transferred to glass weighing bottles and samples for calorimetric measurements were transferred to glass ampoules in the dry box.

Two samples of "$FeCl_2$" that were prepared at different times and handled separately in the dry box were analyzed for Fe^{2+} (dichromate titration) and for Cl^- (gravimetric AgCl) with results that correspond to composition $FeCl_2 \cdot nH_2O$(c) in which $n = 0.0082$ for Sample No. 1 and $n = 0.0228$ for Sample No. 2.

All calorimetric measurements have been made with our LKB 8700 Precision Calorimetry System. The standard LKB 100 ml glass calorimeter vessel was used with 1 ml glass ampoules to contain solid samples to be dissolved. Several "blank" calorimetric runs were made to establish the small heat of breaking. All of our calorimetric results refer to 25.00 ± 0.05°C and are reported in terms of the defined thermochemical calorie (1 cal = 4.184 J).

Enthalpies of solution were determined in 100 ml of distilled water (pH adjusted to 4.0 with dilute hydrochloric acid) through which N_2 was passed by way of a porous frit to ensure the absence of dissolved oxygen. Following completion of each calorimetric run, each solution was checked for presence of Fe^{3+}(aq) by addition of a few drops of potassium thiocyanate solution. Absence of the characteristic red color of the ferric thiocyanate complex confirmed that there had been no oxidation of Fe(II) to Fe(III) in our handling of $FeCl_2$(c) or in the calorimetric solution.

RESULTS AND CALCULATIONS

Results of our calorimetric measurements on Samples Nos. 1 and 2 are summarized in Tables 1 and 2. The ΔH values listed in these Tables have been derived from the measured masses of samples and enthalpies of solution in combination with the molecular weights for the substances represented by $FeCl_2 \cdot nH_2O(c)$. The standard molar enthalpies of solution represented by ΔH° have been derived by combination of individual ΔH values with enthalpies of dilution to infinite dilution. These enthalpies of dilution have been estimated from tabulated enthalpies for aqueous nickel chloride[6] and magnesium chloride[8] over the concentration range of our solutions.

We now proceed to use the ΔH° values given in Tables 1 and 2 that refer to $FeCl_2 \cdot nH_2O(c)$ to obtain the desired ΔH° that will refer to the standard enthalpy of solution of anhydrous $FeCl_2(c)$.

Results of older investigations cited by Bichowsky and Rossini[9] and in NBS Circ. 500[5] demonstrate the existence of two hydrates of ferrous chloride: $FeCl_2 \cdot 2H_2O(c)$ and $FeCl_2 \cdot 4H_2O(c)$. We can therefore consider our $FeCl_2 \cdot nH_2O(c)$ samples with $n \ll 1$ to be appropriate mixtures of $FeCl_2(c)$ and $FeCl_2 \cdot 2H_2O(c)$. On this basis we calculate that one mole of Sample No. 1 consisted of 0.9959 mole of

TABLE 1

ENTHALPIES OF SOLUTION OF $FeCl_2 \cdot 0.0082H_2O(c)$

g of sample	ΔH(kcal mol^{-1})	ΔH°(kcal mol^{-1})
0.046948	−19.65	−19.78
0.027942	−19.73	−19.83
0.044313	−19.66	−19.79
0.051329	−19.66	−19.80
0.026774	−19.70	−19.80
0.085445	−19.59	−19.76

TABLE 2

ENTHALPIES OF SOLUTION OF $FeCl_2 \cdot 0.0228H_2O(c)$

g of sample	ΔH(kcal mol^{-1})	ΔH°(kcal mol^{-1})
0.200275	−19.43	−19.71
0.066425	−19.50	−19.65
0.148816	−19.40	−19.64
0.055823	−19.52	−19.67

$FeCl_2$(c) and 0.0041 mole of $FeCl_2 \cdot 2H_2O$(c). Similarly, one mole of Sample No. 2 consisted of 0.9882 mole of $FeCl_2$(c) and 0.0118 mole of $FeCl_2 \cdot 2H_2O$(c)

The calorimetric results cited by Bichowsky and Rossini[9] in combination with estimated heat capacities and enthalpies of dilution lead us to $\Delta H^\circ = -9.9$ kcal mol^{-1} for the standard enthalpy of solution of $FeCl_2 \cdot 2H_2O$(c). We estimate that the uncertainty in this value is slightly less than ± 1 kcal mol^{-1}. We may also use the vapor pressure results of Schäfer[10] with the enthalpy of vaporization of water and an approximate enthalpy of solution of $FeCl_2$(c) to obtain $\Delta H^\circ = -10.8$ kcal mol^{-1} for the standard enthalpy of solution of $FeCl_2 \cdot 2H_2O$. The uncertainty in this value is probably more than ± 1 kcal mol^{-1}. We adopt $\Delta H^\circ = -10$ kcal mol^{-1} for the enthalpy of solution of $FeCl_2 \cdot 2H_2O$(c).

We now express the average $\Delta H^\circ = -19.79$ kcal mol^{-1} for dissolving Sample No. 1 as

$$-19.79 = 0.9959\Delta H^\circ_a + 0.0041\Delta H^\circ_b \qquad (2)$$

in which ΔH°_a represents the desired standard enthalpy of solution of anhydrous $FeCl_2$(c) and $\Delta H^\circ_b = -10$ kcal mol^{-1} is the enthalpy of solution of the hydrate $FeCl_2 \cdot 2H_2O$(c). From eqn (2) we obtain $\Delta H^\circ_a = -19.83$ kcal mol^{-1}.

Changing the value of ΔH°_b by 1 kcal mol^{-1} changes the calculated value of ΔH°_a by less than 0.01 kcal mol^{-1}.

Similarly for Sample No. 2 we have

$$-19.67 = 0.9882\,\Delta H^\circ_a + 0.0118\,\Delta H^\circ_b \qquad (3)$$

and thence $\Delta H^\circ_a = -19.79$ kcal mol^{-1}. In this case, changing the value of ΔH°_b by 1 kcal mol^{-1} changes the calculated value of ΔH°_a by 0.012 kcal mol^{-1}.

The vapor pressure results of Schäfer[10] that we have already cited and used in connection with $FeCl_2 \cdot 2H_2O$(c) point toward the existence of $FeCl_2 \cdot H_2O$(c) as well as the higher hydrates already mentioned. On this basis we can consider our $FeCl_2 \cdot nH_2O$(c) samples with $n \ll 1$ to be mixtures of $FeCl_2$(c) and $FeCl_2 \cdot H_2O$(c); we calculate that one mole of Sample No. 1 consisted of 0.9918 mole of $FeCl_2$(c) and 0.0082 mole of $FeCl_2 \cdot H_2O$(c) and that one mole of Sample No. 2 consisted of 0.9772 mole of $FeCl_2$(c) and 0.0228 mole of $FeCl_2 \cdot H_2O$(c).

Combination of the vapor pressure results of Schäfer[10] with the enthalpy of vaporization of water and an approximate enthalpy of solution of $FeCl_2$(c) leads to $\Delta H^\circ_b = -15$ kcal mol^{-1} (probably ± 2 kcal mol^{-1}) for the enthalpy of solution of $FeCl_2 \cdot H_2O$(c).

We now express the average ΔH° for dissolving Sample No. 1 as

$$-19.79 = 0.9918\,\Delta H^\circ_a + 0.0082\,\Delta H^\circ_b \qquad (4)$$

in which ΔH°_a is again the desired enthalpy of solution of anhydrous $FeCl_2$(c) and $\Delta H^\circ_b = -15$ kcal mol^{-1}. From eqn (4) we obtain $\Delta H^\circ_a = -19.83$ kcal mol^{-1}. Changing the value of ΔH°_b by 2 kcal mol^{-1} changes the calculated ΔH°_a by 0.02 kcal mol^{-1}.

Similarly for Sample No. 2 we have

$$-19.67 = 0.9772\,\Delta H_a^\circ + 0.0228\,\Delta H_b^\circ \qquad (5)$$

and thence $\Delta H_a^\circ = -19.78$ kcal mol^{-1}. Changing ΔH_b° by 2 kcal mol^{-1} changes the calculated value of ΔH_a° by 0.05 kcal mol^{-1}.

Weighting the results for Sample No. 1 more than those for Sample No. 2 leads us to select $\Delta H^\circ = -19.82$ kcal mol^{-1} as the "best" standard enthalpy for dissolving anhydrous $FeCl_2$(c). Our considerations of uncertainties in sample compositions, our calorimetric measurements, and auxiliary quantities we have used in our calculations lead us to estimate that the total uncertainty in this "best" ΔH° is no more than ± 0.10 kcal mol^{-1}.

The only enthalpies of solution of "$FeCl_2$(c)" that we know of that are worth comparing with our "best" result above are from Li and Gregory[11] who have made five measurements with final concentrations ranging from 0.00139 to 0.0117 mol kg^{-1}. Combination of their reported ΔH values with the enthalpies of dilution we used in obtaining ΔH° values from our measured ΔH values leads us to an average $\Delta H^\circ = -19.7$ kcal mol^{-1} for the standard enthalpy of solution of "$FeCl_2$(c)". Because we have no analytical data to justify further calculations to allow for a small amount of $FeCl_2 \cdot H_2O$(c) or $FeCl_2 \cdot 2H_2O$(c) in their samples, we can only note that presence of a small amount of hydrate would lead to a ΔH° for dissolving anhydrous $FeCl_2$(c) that is slightly more negative than the -19.7 kcal mol^{-1} given above, and thence in better agreement with our $\Delta H^\circ = -19.82$ kcal mol^{-1}.

We use $\Delta H_f^\circ = -39.952$ kcal mol^{-1} for Cl^-(aq) from NBS Tech. Note 270-3[12] in combination with our $\Delta H^\circ = -19.82$ kcal mol^{-1} for the standard enthalpy of solution of $FeCl_2$(c) to obtain

$$\Delta H_f^\circ[Fe^{2+}(aq)] - \Delta H_f^\circ[FeCl_2(c)] = 60.08 \text{ kcal mol}^{-1} \qquad (6)$$

Now we have a choice between several different calculations of which two follow:

(i) We can adopt $\Delta H_f^\circ = -22.1$ kcal mol^{-1} for Fe^{2+}(aq) as reported by Larson et al.[7] on the basis of their ΔH° of solution of $FeSO_4 \cdot 7H_2O$ and the ΔH_f° of this compound derived from the measurements of Adami and Kelley[13]. In this way we obtain $\Delta H_f^\circ = -82.2$ kcal mol^{-1} for $FeCl_2$(c).

(ii) We can adopt $\Delta H_f^\circ = -81.69$ kcal mol^{-1} for $FeCl_2$(c) from the calorimetric measurements of Koehler and Coughlin[14] in combination with auxiliary thermodynamic properties from NBS Tech. Note 270-3[12]. In this way we obtain $\Delta H_f^\circ = -21.61$ kcal mol^{-1} for Fe^{2+}(aq).

Discrepancies between the selected ΔH_f° values and results of calculations (i) and (ii) are larger than stated uncertainties in the various investigations and can only be resolved by further measurements.

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