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Thermochemistry of inorganic sulfur compounds

V. Peroxymonosulfate revisited: standard molar enthalpies of formation of $KHSO_5 \cdot H_2O$(cr), $KHSO_5$(cr), and HSO_5^-(aq)[a]

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The enthalpy of reaction of pure $KHSO_5 \cdot H_2O$ with HI(aq) has been determined calorimetrically. This result has been combined with auxiliary enthalpy-of-solution measurements to yield the standard molar enthalpy of formation: $\Delta_f H_m^\circ(KHSO_5 \cdot H_2O, \text{cr}, 298.15\ \text{K}) = -(1359.88 \pm 0.57)\ \text{kJ} \cdot \text{mol}^{-1}$. The standard molar enthalpies of solution in water of $KHSO_5 \cdot H_2O$ and $KHSO_5$ have also been measured: $\Delta_{sln} H_m^\circ(KHSO_5 \cdot H_2O, \text{cr}, 298.15\ \text{K}) = (46.24 \pm 0.34)\ \text{kJ} \cdot \text{mol}^{-1}$, $\Delta_{sln} H_m^\circ(KHSO_5, \text{cr}, 298.15\ \text{K}) = (33.68 \pm 0.24)\ \text{kJ} \cdot \text{mol}^{-1}$. From these results, $\Delta_f H_m^\circ(HSO_5^-, \text{aq})$ with standard molality $m^\circ = 1\ \text{mol} \cdot \text{kg}^{-1}$, has been calculated to be $-(775.64 \pm 0.68)\ \text{kJ} \cdot \text{mol}^{-1}$. The standard potential for the aqueous half-reaction: $HSO_5^- + 2H^+ + 2e^- = HSO_4^- + H_2O$, is estimated to be (1.85 ± 0.03) V. Also reported are $\Delta_f H_m^\circ(KHSO_5, \text{cr}, 298.15\ \text{K}) = -(1061.49 \pm 0.71)\ \text{kJ} \cdot \text{mol}^{-1}$; the molar enthalpy of dehydration at 298.15 K for the reaction: $KHSO_5 \cdot H_2O(\text{cr}) = KHSO_5(\text{cr}) + H_2O(\text{l})$, $\Delta_r H_m^\circ = (12.56 \pm 0.42)\ \text{kJ} \cdot \text{mol}^{-1}$; and the equilibrium H_2O(g) vapor pressure at 298.15 K for the dehydration reaction: $KHSO_5 \cdot H_2O(\text{cr}) = KHSO_5(\text{cr}) + H_2O(\text{g})$, $p/p^\circ = (7.1 \pm 1.0) \times 10^{-3}$. Taking $p^\circ = 101325$ Pa, the vapor pressure is (720 ± 100) Pa.

1. Introduction

Peroxymonosulfuric acid, H_2SO_5, is of interest as a powerful and labile oxidant and as an intermediate in the preparation of H_2O_2 by stepwise hydrolysis of peroxydisulfuric acid, $H_2S_2O_8$. Its enthalpy of formation $\Delta_f H_m^\circ(H_2SO_5)$ is also important in judging the feasibility of mechanisms proposed for the formation of sulfuric acid in the polluted atmosphere.(1)

Neat H_2SO_5 is unstable, but in aqueous solution it dissociates as a strong monobasic acid, and the salt $KHSO_5$ has been known for some time, although its characterization is still far from complete. A stable mixed salt of approximate composition $2KHSO_5 \cdot KHSO_4$ is marketed by Du Pont under the trade name OXONE, and a partially purified material derived from this product was used in a

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[a] Work performed under the auspices of the Office of Basic Energy Sciences, U.S. Department of Energy.

recent thermochemical study to obtain a value for the enthalpy of formation of aqueous H_2SO_5.(2)

In the same study, the standard electrode potential of the aqueous half-reaction:

$$HSO_5^-(aq) + 2H^+(aq) + 2e^- = HSO_4^-(aq) + H_2O(l), \qquad (1)$$

was estimated to be 1.82 V. This is considerably higher than the widely accepted values of 1.5 to 1.6 V that have been obtained by electrochemical measurements,(3,4) but it agrees well with a value of 1.81 V that has been calculated from the equilibrium constant for hydrolysis of H_2SO_5:(5)

$$HSO_5^-(aq) + H_2O(l) = HSO_4^-(aq) + H_2O_2(aq). \qquad (2)$$

We have now developed a relatively convenient procedure for the preparation of substantial quantities of the neat hydrated salt $KHSO_5 \cdot H_2O$, and it seemed appropriate to carry out a careful thermochemical study of this compound. The technique chosen for this study was solution calorimetry. We have measured the enthalpy of reaction of the peroxymonosulfate salt with HI(aq) and its enthalpy of solution in water along with other enthalpies of solution required for the calculation of $\Delta_f H_m^\circ(KHSO_5 \cdot H_2O)$. We have found that $KHSO_5 \cdot H_2O$ dehydrates readily when exposed to flowing dry helium, and we have also carried out thermochemical measurements on anhydrous $KHSO_5$.

2. Experimental

MATERIALS

$KHSO_5 \cdot H_2O(cr)$. A concentrated solution of reagent-grade $Na_2S_2O_8$ was converted to $H_2S_2O_8$ by passage through a column of Dowex 50X8 cation-exchange resin in the hydrogen form. The solution was concentrated in a rotary evaporator and hydrolyzed by heating at 323 K until no $S_2O_8^{2-}(aq)$ remained:

$$S_2O_8^{2-}(aq) + H_2O(l) = HSO_5^-(aq) + HSO_4^-(aq). \qquad (3)$$

The absence of $S_2O_8^{2-}(aq)$ was inferred from the lack of slow further oxidation of $I^-(aq)$ after its rapid reaction with the $HSO_5^-(aq)$ formed. Solid $KHCO_3$ was added to the solution in an ice bath to increase the pH to 3.5, the cold solution was filtered from precipitated K_2SO_4, and the filtrate was freeze-dried. The solid residue was redissolved in a small quantity of water at about 295 K, and the solution was filtered. The filtrate was chilled in an ice bath, and the precipitate of impure product was filtered cold, redissolved in a minimal quantity of water at 295 K, and recrystallized several times. The final product precipitate was filtered and dried on a porous porcelain plate. It was stored in a desiccator over saturated $Ca(NO_3)_2(aq)$ until it reached constant mass.

The sample was analyzed for oxidizing power by reaction with excess $I^-(aq)$ in acid solution, followed by titration of the liberated $I_3^-(aq)$ with $Na_2S_2O_3(aq)$ that had been standardized against primary standard-grade KIO_3. Potassium was determined gravimetrically with tetraphenyl boron. The oxidizing power was found to be (100.09 ± 0.14) per cent of that required by the empirical formula

$KHSO_5 \cdot H_2O$, and the K content was (23.2 ± 0.1) mass per cent compared with the theoretical value of 22.97 mass per cent. (The uncertainty corresponds to twice the standard deviation of the mean of the analytical results.) A 0.1 $mol \cdot dm^{-3}$ aqueous solution had $pH > 4$, and potentiometric titration with base indicated that the sample did not contain more than 0.15 mass per cent of $KHSO_4$. A carefully weighed portion of $KHSO_5 \cdot H_2O$ on a Petri dish was exposed to flowing dry helium in a glovebox. After about 24 h, the sample had reached constant mass, having lost 10.55 per cent of the original mass. The theoretical H_2O content of $KHSO_5 \cdot H_2O$ is 10.59 per cent.

The K analysis is not quite consistent with the oxidizing power and the mass loss on drying. However, since it is the least accurate of the analytical results, we have put our reliance on the other analyses and have calculated the calorimetric results on the assumption that the sample was stoichiometric $KHSO_5 \cdot H_2O$ and contained no significant impurities.

$KHSO_5$(cr). This material was prepared by dehydrating $KHSO_5 \cdot H_2O$ in the manner described in the previous paragraph. Potentiometric titration with base showed that the dehydrated material contained about 0.2 mass per cent of $KHSO_4$. The specimen was assumed to be pure $KHSO_5$ and the calorimetric results are based upon that assumption.

Other reagents. High-purity I_2(cr), purchased from Johnson Matthey Chemicals Ltd., was certified to contain less than mass fraction 3×10^{-6} of total metallic impurities. Potassium iodide was Baker Analyzed Reagent, stated assay 100.4 mass per cent, containing 0.02 mass per cent of $(Cl^- + Br^-)$ and 0.001 mass per cent of Na. Before use, it was dried under vacuum at 428 K for 72 h. Potassium sulfate, Johnson Matthey "puratronic" grade, was certified to contain as sole metallic impurities mass fraction 3×10^{-6} of Rb, Na, and Ca; before use it was dried under vacuum at 400 K for 48 h. All the above reagents were stored and weighed in a glovebox filled with circulating high-purity helium. Constant-boiling HI was prepared by several distillations of 48 mass per cent HI from a slight excess of H_3PO_2. Because hydriodic acid oxidizes so readily, it was diluted to the required concentrations with nitrogen-saturated distilled H_2O in an inert atmosphere. The diluted acid was stored under argon in subdued light.

CALORIMETRIC PROCEDURES

Enthalpies of solution and reaction were determined in an LKB–8700 Precision Calorimetric System. Temperatures were measured with a Hewlett-Packard quartz-crystal thermometer (Model 2804–A). A glass reaction vessel and a (stirrer + ampoule-holder) assembly made of KEL–F plastic, both of which are inert to iodine, were used. The reaction and dissolutions went rapidly to completion.

The specific enthalpy of reaction of tris(hydroxymethyl)aminomethane with 0.1 $mol \cdot dm^{-3}$ HCl was found to be $-(245.81 \pm 0.09)$ $J \cdot g^{-1}$; the certified specific enthalpy of reaction is $-(245.76 \pm 0.26)$ $J \cdot g^{-1}$. Thus, the calorimeter and associated measuring devices were judged to be performing satisfactorily.

The $KHSO_5 \cdot H_2O$, $KHSO_5$, KI, and K_2SO_4 were weighed (the $KHSO_5 \cdot H_2O$ in air to avoid loss of water) in glass ampoules of 1 cm^3 internal volume. Measurements leading to $\Delta_f H^\circ_m(KHSO_5 \cdot H_2O)$ were performed in the following sequence (see table 3): $KHSO_5 \cdot H_2O$ was reacted with HI(aq), reaction (1), and KI was dissolved in the resulting solution, reaction (5). Iodine was dissolved in HI(aq), reaction (2), to give a solution identical to that used in previous work at this laboratory.(6) This solution was diluted very slightly, reaction (3), and K_2SO_4 was dissolved in it, reaction (4). Enthalpies of solution of $KHSO_5 \cdot H_2O$ and $KHSO_5$ (table 2) were measured in freshly boiled distilled H_2O.

Dissolutions of KI, K_2SO_4, $KHSO_5$, and $KHSO_5 \cdot H_2O$ were all endothermal. In experiments with these compounds, an accurately measured quantity of electrical energy was supplied to the calorimeter such that the corrected temperature change was very small; it was calculated as outlined in reference 7. For all calorimetric experiments, the mean temperature of the calorimeter was (298.15 ± 0.02) K.

3. Results

Calorimetric results are given in tables 1 and 2. The column headings have the following meanings: ⟨ε(calor)⟩ is the mean energy equivalent of the calorimetric

TABLE 1. Calorimetric results (T = 298.15 K) for reactions of $KHSO_5 \cdot H_2O$, KI, and α-K_2SO_4

Expt no.	$\frac{\langle\varepsilon(\text{calor})\rangle}{J \cdot K^{-1}}$	$\frac{\Delta\theta_c}{K}$	$\frac{\langle\varepsilon(\text{calor})\rangle(-\Delta\theta_c)}{J}$	$\frac{\Delta_{vap}H}{J}$	$\frac{\Delta_{elec}H}{J}$	$\frac{m}{g}$	$\frac{\Delta H_m/M}{J \cdot g^{-1}}$
			$KHSO_5 \cdot H_2O$				
6	447.79	0.64071	−286.904	−0.051		0.20623	−1391.4
5	447.25	0.64805	−289.840	−0.051		0.20851	−1390.3
4	447.22	0.64451	−288.238	−0.051		0.20764	−1388.4
3	447.22	0.64477	−288.354	−0.051		0.20727	−1391.4
2	447.23	0.65118	−291.227	−0.051		0.20956	−1390.0
			$\langle\Delta H_m/M\rangle = -(1390.3 \pm 0.6)\ J \cdot g^{-1}$ [a]				
			KI				
1	443.77	0.00541	−2.401	−0.052	27.041	0.19847	123.89
2	444.06	−0.00122	0.542	−0.052	24.537	0.20367	122.88
3	443.49	0.00034	−0.151	−0.052	25.038	0.20162	123.18
4	443.35	0.00036	−0.160	−0.052	25.038	0.20352	121.98
5	443.50	0.00014	−0.062	−0.052	25.037	0.20295	122.80
6	443.20	−0.00042	0.186	−0.052	25.038	0.20202	124.60
			$\langle\Delta H_m/M\rangle = (123.22 \pm 0.37)\ J \cdot g^{-1}$ [a]				
			α-K_2SO_4				
1	443.6 [b]	−0.05299	23.506	−0.052	29.043	0.21350	245.89
2	443.6	−0.00344	1.526	−0.052	50.074	0.20938	246.19
3	443.6	−0.00385	1.708	−0.052	50.074	0.21014	246.17
4	443.6	−0.00388	1.721	−0.052	50.074	0.21055	245.75
5	443.6	−0.00614	2.724	−0.052	50.074	0.21560	244.65
			$\langle\Delta H_m/M\rangle = (245.73 \pm 0.28)\ J \cdot g^{-1}$ [a]				

[a] Mean values with uncertainties given as standard deviations of the mean.

[b] Estimated value based on the other ⟨ε(calor)⟩ values given in the table.

TABLE 2. Enthalpies of solution of $KHSO_5 \cdot H_2O$(cr) and of $KHSO_5$(cr) in H_2O(l) at 298.15 K

Expt no.	$\Delta_{elec}H$ / J	$\Delta\theta_c$ / K	$\langle\varepsilon(\text{calor})\rangle(-\Delta\theta_c)$ [a] / J	$\Delta_{vap}H$ / J	m / g	$\Delta H_m/M$ / $J \cdot g^{-1}$	$\langle\Delta H_m/M\rangle$ / $J \cdot g^{-1}$
			$KHSO_5 \cdot H_2O$				
7	47.073	−0.02099	9.481	−0.051	0.20868	270.8	(271.4 ± 0.2)[b,c]
8	55.087	−0.00443	2.001	−0.051	0.20977	271.9	
9	55.086	−0.00362	1.635	−0.051	0.20905	271.1	
10	55.086	−0.00253	1.143	−0.051	0.20670	271.8	
11	55.086	−0.00229	1.034	−0.051	0.20675	271.2	
12	30.048	−0.00051	0.230	−0.054	0.11109	272.1	(271.9 ± 0.2)[b,d]
13	29.547	0.00014	−0.063	−0.054	0.10828	271.8	
14	8.013	0.00053	−0.239	−0.056	0.02874	268.5	(271.7 ± 1.0)[b,c]
15	8.513	−0.00057	0.257	−0.056	0.03190	273.2	
16	8.013	−0.00085	0.384	−0.056	0.03030	275.3	
17	8.012	0.00032	−0.145	−0.056	0.02879	271.3	
18	8.012	0.00019	−0.086	−0.056	0.02897	271.7	
19	8.012	−0.00048	0.217	−0.056	0.03025	270.2	
			$KHSO_5$				
1	40.063	−0.00099	0.447	−0.052	0.18417	219.7	(221.3 ± 1.6)[b,d]
2	41.065	−0.00123	0.556	−0.052	0.18663	222.7	
3	42.067	0.00046	−0.208	−0.052	0.18868	221.6	
4	41.566	0.00040	−0.181	−0.052	0.18672	221.4	

[a] The mean energy equivalent of the calorimetric system, $\langle\varepsilon(\text{calor})\rangle = 451.7\ J \cdot K^{-1}$, is based on separate experiments.

[b] Mean final compositions of the solutions were $KHSO_5 \cdot 4544H_2O$, $KHSO_5 \cdot 8624H_2O$, and $KHSO_5 \cdot 31712H_2O$ for experiments 7 to 11, 12 and 13, and 14 to 19, respectively, and $KHSO_5 \cdot 4534H_2O$ for the experiments with $KHSO_5$.

[c] Uncertainty is the standard deviation of the mean.

[d] Estimated uncertainty.

system based on electrical calibrations; $\Delta\theta_c$ is the corrected temperature change of the calorimeter; $\Delta_{vap}H$ is the correction for saturating the free volume of the ampoules with water vapor; $\Delta_{elec}H$ is the electrical energy supplied to the calorimetric system; m is the mass compound reacted or dissolved; and $\Delta H_m/M$ is the specific enthalpy of reaction or solution.

The thermochemical cycle for the derivation of $\Delta_f H^\circ_m(KHSO_5 \cdot H_2O$, cr, 298.15 K) is given in table 3. Uncertainties are twice the standard deviations of the mean. The enthalpies of reactions (1), (4), and (5) are taken from table 1 and are based on molar masses of 170.18, 174.26, and 163.003 $g \cdot mol^{-1}$ for $KHSO_5 \cdot H_2O$, K_2SO_4, and KI, respectively. The enthalpy of reaction (2) was measured previously at this laboratory(6) and was later recalculated,(8) and for reactions (3), (6), and (7) we used the selected enthalpies of dilution of HI(aq)(9) and $\Delta_f H^\circ_m(I^-$, aq) $= -(56.785 \pm 0.071)$ $kJ \cdot mol^{-1}$.(8)† The standard molar enthalpies of formation, reactions (8), (9), and (10), are based upon the standard molar enthalpies of solution of α-K_2SO_4: $(23.75 \pm 0.08)\ kJ \cdot mol^{-1}$,(10) and of KI: $(20.33 \pm 0.12)\ kJ \cdot mol^{-1}$,(9) and upon the standard molar enthalpies of formation of $K^+(aq) = -(252.17 \pm 0.10)\ kJ \cdot mol^{-1}$,(11)

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† Throughout this paper the standard molality $m^\circ = 1\ mol \cdot kg^{-1}$.

TABLE 3. Thermochemical cycle for derivation of $\Delta_f H_m^\circ(KHSO_5 \cdot H_2O, cr, 298.15 K)$[a]

Reaction	$\Delta_r H_m/(kJ \cdot mol^{-1})$
1. sln A = $KHSO_5 \cdot H_2O(cr) + 15.403(HI \cdot 290.651H_2O)$	236.60 ± 0.20
2. $I_2(cr) + 14.403(HI \cdot 310.90H_2O)$ = sln B	5.08 ± 0.11
3. $H_2O(l)$ + sln B = sln C	0.00 ± 0.00
4. $K_2SO_4(cr, \alpha)$ + sln C = sln D	42.82 ± 0.10
5. sln D = $KI(cr)$ + sln A	-20.45 ± 0.12
6. $14.403(HI \cdot 290.651H_2O) + 291.65H_2O(l) = 14.403(HI \cdot 310.90H_2O)$	-0.13 ± 0.02
7. $HI \cdot 290.651H_2O = \frac{1}{2}H_2(g) + \frac{1}{2}I_2(cr) + 290.651H_2O(l)$	56.26 ± 0.07
8. $2K(cr) + S(cr, rh) + 2O_2(g) = K_2SO_4(cr, \alpha)$	-1437.69 ± 0.45
9. $KI(cr) = K(cr) + \frac{1}{2}I_2(cr)$	329.29 ± 0.18
10. $2H_2(g) + O_2(g) = 2H_2O(l)$	-571.66 ± 0.08
11. $K(cr) + \frac{3}{2}H_2(g) + 3O_2(g) + S(cr, rh) = KHSO_5 \cdot H_2O(cr)$	-1359.88 ± 0.57

[a] Compositions of acids are given to more significant figures than is justified; this is done solely to insure that the stoichiometric numbers for H_2O completely cancel out in the cycle. In the table, sln A = $K^+ \cdot HSO_4^- \cdot 13.403H^+ \cdot I_3^- \cdot 14.403I^- \cdot 4478.89H_2O$; sln B = $14.403H^+ \cdot I_3^- \cdot 13.403I^- \cdot 4477.89H_2O$; sln C = $14.403H^+ \cdot I_3^- \cdot 13.403I^- \cdot 4478.89H_2O$; sln D = $2K^+ \cdot HSO_4^- \cdot 13.403H^+ \cdot I_3^- \cdot 13.403I^- \cdot 4478.89H_2O$.

$SO_4^{2-}(aq) = -(909.60 \pm 0.40)\ kJ \cdot mol^{-1}$,(11) $I^-(aq)$,(8) and $H_2O(l)$.(11) The standard molar enthalpy of formation, $\Delta_f H_m^\circ(KHSO_5 \cdot H_2O$, cr, 298.15 K), is thus calculated to be $-(1359.88 \pm 0.57)\ kJ \cdot mol^{-1}$, where the uncertainty is the square root of the sum of the squares of the uncertainties of the enthalpies of reactions (1) through (10).

Enthalpy-of-solution results for $KHSO_5 \cdot H_2O$ are given in the upper part of table 2. It appears that within the limits of accuracy of our measurements and for the compositions studied the enthalpies of solution are independent of the composition of $KHSO_5(aq)$. It is on that basis that we assume (table 4) the enthalpy of dilution to be essentially zero. Inserting $\Delta_f H_m^\circ(K^+, aq) = -(252.17 \pm 0.10)\ kJ \cdot mol^{-1}$,(11) into reaction (5) (table 4), we obtain $\Delta_f H_m^\circ(HSO_5^-, aq) = -(775.64 \pm 0.68)\ kJ \cdot mol^{-1}$.

The standard electrode potential for the aqueous half-reaction given in equation (1) has been calculated as follows. First of all, $S_m^\circ(HSO_5^-$, aq) had to be estimated. For that purpose, we used the formula of Connick and Powell,(12) taking *n*, the number of charge-bearing ligands equal to 4, and obtain $S_m^\circ(HSO_5^-, aq) = (205 \pm 20)$

TABLE 4. Thermochemical cycle for calculation of $\Delta_f H_m^\circ(HSO_5^-$, aq, 298.15 K) ($m^\circ = 1\ mol \cdot kg^{-1}$)

1. $KHSO_5 \cdot H_2O(cr) + 31711H_2O(l) = KHSO_5 \cdot 31712H_2O$; $\Delta_r H_m = (46.24 \pm 0.34)\ kJ \cdot mol^{-1}$ [a]
2. $KHSO_5 \cdot 31712H_2O + (\infty - 31712)H_2O(l) = K^+(aq, \infty) + HSO_5^-(aq, \infty)$; $\Delta_r H_m = (0.00 \pm 0.10)\ kJ \cdot mol^{-1}$ [a]
3. $H_2O(l) = H_2(g) + \frac{1}{2}O_2(g)$; $\Delta_r H_m^\circ = (285.83 \pm 0.04)\ kJ \cdot mol^{-1}$ [b]
4. $K(cr) + \frac{3}{2}H_2(g) + S(cr, rh) + 3O_2(g) = KHSO_5 \cdot H_2O(cr)$; $\Delta_r H_m^\circ = -(1359.88 \pm 0.57)\ kJ \cdot mol^{-1}$ [c]
5. $K(cr) + \frac{1}{2}H_2(g) + S(cr, rh) + 2\frac{1}{2}O_2(g) + \infty H_2O(l) = K^+(aq, \infty) + HSO_5^-(aq, \infty)$; $\Delta_r H_m^\circ = -(1027.81 \pm 0.67)\ kJ \cdot mol^{-1}$

[a] From table 2. [b] Reference 11. [c] From table 3.

$J \cdot K^{-1} \cdot mol^{-1}$. This estimate combined with S°_m values for $HSO_4^-(aq)$,[13] $H_2O(l)$,[11] and $H_2(g)$,[11] leads to $\Delta_r S^\circ_m = -(134 \pm 20)\ J \cdot K^{-1} \cdot mol^{-1}$ for reaction (1). Taking $\Delta_f H^\circ_m$ values of $-(887.34 \pm 1.4)\ kJ \cdot mol^{-1}$,[13] $-(285.83 \pm 0.04)\ kJ \cdot mol^{-1}$,[11] and $-(775.64 \pm 0.68)\ kJ \cdot mol^{-1}$ for $HSO_4^-(aq)$, $H_2O(l)$, and $HSO_5^-(aq)$, respectively, we calculate $\Delta_r G^\circ_m = -(357.58 \pm 6.16)\ kJ \cdot mol^{-1}$. The derived standard electrode potential is (1.85 ± 0.03) V at 298.15 K, taking $F = 96487\ C \cdot mol^{-1}$.

The lower part of table 2 gives calorimetric results for the dissolution of anhydrous $KHSO_5$ (molar mass: $152.17\ g \cdot mol^{-1}$). These values are assumed to be valid for infinite dilution and, when combined with those for $KHSO_5 \cdot H_2O$ (top section of table 2), give $\Delta_r H^\circ_m = (12.56 \pm 0.42)\ kJ \cdot mol^{-1}$ for the dehydration reaction:

$$KHSO_5 \cdot H_2O(cr) = KHSO_5(cr) + H_2O(l); \qquad (4)$$

thus, with $\Delta_f H^\circ_m(H_2O, l)$[21] we deduce $\Delta_f H^\circ_m(KHSO_5, cr, 298.15\ K) = -(1061.49 \pm 0.71)\ kJ \cdot mol^{-1}$. For dehydration to $H_2O(g)$ at 298.15 K:

$$KHSO_5 \cdot H_2O(cr) = KHSO_5(cr) + H_2O(g), \qquad (5)$$

we calculate $\Delta_r H^\circ_m = (56.58 \pm 0.42)\ kJ \cdot mol^{-1}$. The difference between the standard molar entropies of $KHSO_5 \cdot H_2O$ and $KHSO_5$ is estimated to be $(40 \pm 8)\ J \cdot K^{-1} \cdot mol^{-1}$ at 298.15 K, based on a comparison of assessed values[13] for analogous compounds. With $S^\circ_m(H_2O, g, 298.15\ K) = (188.72 \pm 0.04)\ J \cdot K^{-1} \cdot mol^{-1}$,[11] $\Delta_r G^\circ_m$ for reaction (5) is calculated to be $(12.25 \pm 2.42)\ kJ \cdot mol^{-1}$ and $K = p/p^\circ = (7.1 \pm 1.0) \times 10^{-3}$. Taking $p^\circ = 101325$ Pa, the equilibrium water vapor pressure is estimated to be about 720 Pa. This estimate is consistent with our ability to equilibrate $KHSO_5 \cdot H_2O$ with water vapor over saturated $Ca(NO_3)_2(aq)$ the equilibrium vapor pressure of which is approximately 1.6 kPa at 298.15 K.[14]

4. Discussion

Our derived value for $\Delta_f H^\circ_m(HSO_5^-, aq)$ is about $23\ kJ \cdot mol^{-1}$ less negative than that reported by Steele and Appelman.[2] The peroxymonosulfate specimen used by Steele and Appelman was not pure (it contained about 74 mass per cent of $KHSO_5$ and about 26 mass per cent of $K_2S_2O_8$, $KHSO_4$, K_2SO_4, $MgSO_4$, and H_2O), and because of that they found it more convenient to determine $\Delta_f H^\circ_m$ of $HSO_5^-(aq)$ rather than of $KHSO_5(cr)$. One element of the thermochemical cycle leading to $\Delta_f H^\circ_m(HSO_5^-, aq)$ involved the enthalpy of solution of the peroxymonosulfate sample in HI(aq). Since peroxymonosulfate reacts with HI(aq), this value cannot be determined experimentally and it was, therefore, assumed to be equal to the enthalpy of solution in $H_2SO_4(aq)$ of the same ionic strength. We suggest that this assumption may be invalid and, consequently, the derived $\Delta_f H^\circ_m(HSO_5^-, aq)$ may well be considerably in error. In contrast, the present measurements were performed on pure $KHSO_5 \cdot H_2O$, and we believe the $\Delta_f H^\circ_m(HSO_5^-, aq)$ result to be definitive.

The electrode potential for reaction (1) has been reported to be 1.47 V by Fichter and Goldach[3] and 1.61 V by Csányi.[4] However, Spiro[5] has shown these potentials to be unreliable and has used the equilibrium constant for reaction (2) estimated by Monger and Redlich(15) to obtain a considerably higher value of 1.81 V. The earlier calorimetric investigation(2) gave a similar potential, 1.82 V, but this agreement is fortuitous because of offsetting errors in the $\Delta_f H_m^\circ$ and estimated S_m° values used for HSO_5^-(aq). We believe our result (1.85 ± 0.03) V to be accurate within the stated error. Nevertheless, we plan to determine the aqueous solubility—and thus $\Delta_{sln} G_m^\circ$—and the low-temperature heat capacity—and thus S_m°—of $KHSO_5$, and in that way calculate an unequivocal value for $S_m^\circ(HSO_5^-, aq)$ and a definitive electrode potential for reaction (1).

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