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THERMODYNAMIC PROPERTIES OF POTASSIUM METASILICATE (K_2SiO_3)

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ABSTRACT

The standard enthalpy of formation of potassium metasilicate (K_2SiO_3), determined by hydrofluoric acid solution calorimetry, was found to be $\Delta H^0_{f,298} = -363.866 \pm 0.421$ kcal mol^{-1} (-1522.415 ± 1.762 kJ mol^{-1}). The standard enthalpy of formation from the oxides was found to be $\Delta H^0_{298} = -64.786 \pm 0.559$ kcal mol^{-1} (-271.065 ± 2.339 kJ mol^{-1}).

These experimentally determined data were combined with data from the literature to calculate the Gibbs energies of formation and equilibrium constants of formation over the temperature range of the literature data. The standard enthalpies of formation and Gibbs energies of formation are given as functions of temperature. The standard Gibbs energy of formation is $\Delta G^0_{f,298.15} = -341.705$ kcal mol^{-1} (-1429.694 kJ mol^{-1}).

INTRODUCTION

Enthalpy of formation values for potassium metasilicate (K_2SiO_3) have been presented by Chase et al. [1]. An unpublished value determined by Hutton et al. at the Dow Chemical Co. used KOH in the reaction scheme. A suitable KOH sample was not available for verifying the reported value; therefore, a determination was made using spectrographically pure KCl.

EXPERIMENTAL

Materials

The acids used, hydrofluoric and hydrochloric, were reagent-grade products that were diluted with distilled water to the proper strength. The KCl was very pure reagent-grade material that was dried at 125 °C before use. The K_2SiO_3 was the same material prepared for and described in an earlier study [2]. The SiO_2 used was from an exceedingly clear and pure single quartz crystal. The crystal was sawed, crushed, ground to pass a 400-mesh

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screen, and elutriated in distilled water. The size fraction ranging between 10 and 20 μm was reserved for the heat of solution determinations. It was repeatedly leached with hydrochloric acid until the solution remained clear, digested with hydrogen peroxide, dried, and heated through the alpha–beta transition before use for each reaction.

Techniques

The enthalpy of formation of K_2SiO_3 was determined by hydrofluoric acid solution calorimetry. The solvent used was 948.7 g of a 20 wt.% hydrofluoric acid–5 wt.% hydrochloric acid mixture. Descriptions of the apparatus have been published elsewhere [3–5]. The quantities of all reacting substances were stoichiometric with 0.742 g of quartz.

The hygroscopic K_2SiO_3 was loaded into preweighed polytetrafluoroethylene tape capsules in a helium-atmosphere dry box, sealed with paraffin, weighed, then sealed in separate containers and stored at constant temperature until use. Immediately before dropping the sample into the calorimeter, the capsules were inserted into a gold-ballasted retaining capsule that held the sample immersed during the solution reaction. All introduced reactants were preweighed and placed in similarly sealed capsules, stored at 25 °C, and dropped into the calorimeter at the appropriate time.

The results of measurements made for the reactions listed in the reaction scheme (Table 1) are listed in Table 2, together with the mean and the uncertainty of the mean for each compound. When several heat of solution values were determined for a reaction, the precision uncertainty was taken as

TABLE 1

Reaction scheme [a] for potassium metasilicate (K_2SiO_3) [b]

Reaction	ΔH (kcal)	Uncertainty (kcal)
(1) $SiO_2(c) + 6HF(sol) \rightarrow H_2SiF_6(sol) + 2H_2O(sol)$	−34.522	±0.011
(2) $26.462H_2O(l) \rightarrow 26.462H_2O(sol)$	18.947	±0.026
(3) $2KCl(c) \rightarrow 2K^+(sol) + 2Cl^-(sol)$	3.846	±0.010
(4) $2(HCl \cdot 12.731H_2O)(l) \rightarrow 2H^+(sol) + 2Cl^-(sol) + 25.462H_2O(sol)$	20.638	±0.034
(5) $K_2SiO_3(c) + 6HF(sol) + 2H^+(sol) \rightarrow 2K^+(sol) + H_2SiF_6(sol) + 3H_2O(sol)$	−85.766	±0.189
$\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$		
(6) $SiO_2(c) + 2KCl(c) + 26.462H_2O(l) \rightarrow K_2SiO_3(c) + 2(HCl \cdot 12.731H_2O)(l)$		
$\Delta H_6 = +53.399 \pm 0.194$		

[a] Symbols c, l, and sol in parentheses denote substances that are crystalline, liquid, or in solution, respectively, in all reactions. [b] For reactions 1–5, introduced reactants are at 25 °C and reaction products are at 73.7 °C.

TABLE 2

Experimental heats of solution

SiO_2(c) reaction 1	H_2O(l) reaction 2	KCl(c) reaction 3	$HCl \cdot 12.731H_2O$(l) reaction 4	K_2SiO_3(c) reaction 5
−34.538	0.715	1.916	10.351	−85.620
−34.527	0.716	1.922	10.290	−86.118
−34.503	0.716	1.926	10.312	−85.854
−34.527	0.714	1.936	10.318	−85.564
−34.527	0.719	1.920	10.333	−85.910
−34.509	0.716	1.923	10.307	−85.531
		1.916		
−34.522	0.716	1.923	10.319	−85.766
±0.011	±0.001	±0.005	±0.017	±0.189

$2[\Sigma d_i^2/n(n-1)]^{1/2}$, where Σd_i^2 is the sum of the squares of the deviations from the mean value and n is the number of determinations; when the heats of two or more reactants were added, the uncertainty was taken as the square root of the sum of the squares of the uncertainties for the individual reactions. These procedures followed the recommendations of Rossini and Deming [6].

All energy units are expressed in terms of the defined calorie (1 cal = 4.1840 J). Weights were corrected to vacuum, and the molecular weights are in accordance with the 1981 table of atomic weights [7]. Final values are rounded to 0.01 kcal. All calibrations are traceable to the National Bureau of Standards (NBS), and sample temperatures are based on the International Practical Temperature Scale of 1968 (IPTS-68) [8].

By maintaining the stoichiometry, the final solution after conducting reactions 1, 2, and 3 consecutively in the original charge of acid was identical to the solution obtained after conducting reactions 4 and 5 consecutively in another charge of acid. The overall calorimetric reaction, reaction 6, may therefore be calculated.

CALCULATIONS

Standard enthalpies of formation

The calculation of the standard enthalpy of formation of K_2SiO_3 requires enthalpy of formation data from the literature for KCl, SiO_2, H_2O, $HCl \cdot 12.371\ H_2O$, and K_2O. The formation reactions for these compounds—reactions 7, 8, 9, 10, and 12—with their enthalpies and precision uncertainties

TABLE 3

Enthalpy of formation of potassium metasilicate

Reaction	$\Delta H^0_{f,198}$ (kcal mol^{-1})	Uncertainty (kcal)	Reference
(7) $K(c)+0.5Cl_2(g) \rightarrow KCl(c)$	−104.385	0.06	10
(8) $Si(c)+O_2(g) \rightarrow SiO_2(c)$	−217.72	0.34	9
(9) $H_2(g)+0.5O_2(g) \rightarrow H_2O(l)$	−68.315	0.01	9
(10) $0.5\ H_2(g)+0.5Cl_2(g)+12.731H_2O(l) \rightarrow HCl \cdot 12.731\ H_2O(l)$	−38.82	0.05	11
$\Delta H_{11} = \Delta H_6 + 2\Delta H_7 + \Delta H_8 + \Delta H_9 - 2\Delta H_{10}$			
(11) $2K(c)+Si(c)+1.5O_2(g) \rightarrow K_2SiO_3(c)$ $\Delta H_{11} = -363.766 \pm 0.421$			
(12) $2K(c)+0.5O_2(g) \rightarrow K_2O(c)$	−81.26	0.5	9
$\Delta H_{13} = \Delta H_6 + 2\Delta H_7 + \Delta H_9 - 2\Delta H_{10} - \Delta H_{12}$			
(13) $SiO_2(c)+K_2O(c) \rightarrow K_2SiO_3(c)$ $\Delta H_{13} = -64.786 \pm 0.559$			

are presented in Table 3 along with the source references. The combination of these reactions, as indicated, provides the formation reaction 11 (Table 3).

$$2K(c) + Si(c) + 1.5O_2(g) \rightarrow K_2SiO_3(c)$$

TABLE 4

Standard formation data for potassium metasilicate for the reaction $2K(c,l,g) + Si(c,l) + 1.5O_2(g) = K_2SiO_3(c)$

T (K)	ΔH^0_f (kcal mol^{-1})	ΔG^0_f (kcal mol^{-1})	log K_f
298.15	−363.766	−341.705	250.474
300	−363.768	−341.568	248.829
336.35 [a]	−363.830	−338.875	220.188
336.35	−364.946	−338.875	220.188
400	−365.000	−333.937	182.452
500	−364.931	−326.175	142.569
600	−364.716	−318.441	115.991
700	−364.385	−310.757	97.021
800	−363.957	−303.126	82.809
900	−363.436	−295.545	71.767
1,000	−362.832	−288.033	62.949
1,043.70 [b]	−362.546	−284.769	59.630
1,043.70	−400.622	−284.769	59.630
1,100	−399.966	−278.539	55.340
1,200	−398.721	−267.559	48.729
1,249	−398.069	−262.213	45.881

[a] Melting point of K. [b] Boiling point of K.

for which the standard enthalpy of formation is

$$\Delta H^0_{f,298} = -363.766 \pm 0.421 \text{ kcal mol}^{-1}$$

The standard enthalpy of formation from the oxides may be determined according to the indicated scheme, which yields the formation reaction 13 (Table 3)

$$SiO_2(c) + K_2O(c) \rightarrow K_2SiO_2(c)$$

for which

$$\Delta H^0_{298}(\text{from oxides}) = -64.786 \pm 0.559 \text{ kcal mol}^{-1}$$

Equilibrium constants of formation

The experimentally determined enthalpy of formation presented here, along with the low-temperature heat capacity, high-temperature thermal data (presented by Beyer et al. [2]), and other necessary data for the constituent elements and oxides [9,10], may be combined to calculate the enthalpies, Gibbs energies of formation, and other relevant properties as a function of temperature. The thermodynamic properties for the formation of potassium metasilicate from the elements and oxides are presented in Tables 4 and 5, respectively.

TABLE 5

Standard formation data from the oxides for potassium metasilicate for the reaction $K_2O(c) + SiO_2(c) = K_2SiO_3(c)$

T (K)	ΔH^0_f (kcal mol^{-1})	ΔG^0_f (kcal mol^{-1})	log K_f
298.15	−64.786	−64.950	47.609
300	−64.787	−64.951	47.316
400	−64.836	−64.999	35.513
500	−64.920	−65.031	28.425
600	−65.026	−65.042	23.691
700	−65.144	−65.040	20.306
800	−65.294	−65.016	17.761
847 [a]	−65.432	−64.995	16.770
847	−65.607	−64.994	16.770
900	−65.610	−64.950	15.772
1,000	−65.554	−64,885	14,180
1,100	−65.429	−64.820	12,878

[a] $\alpha-\beta$ transition point of quartz.

DISCUSSION

The only experimentally determined enthalpy of formation value for potassium metasilicate found in the literature was reported by Chase et al. [1]. Their value, $\Delta H^0_{f,298} = -369.9 \pm 1.0$ kcal mol^{-1}, was in good agreement with other calculated and estimated values. The difference between this value and the one reported here ($\Delta H^0_{f,298} = -363.8 \pm 0.4$ kcal mol^{-1}) is probably due to inconsistencies between the values for KOH and KCl. The more recent value used for K_2O (reaction 12, Table 3), $\Delta H^0_{f,298} = -81.26$ kcal mol^{-1} [9], is preferred to the value reported earlier, $\Delta H^0_{f,298} = -86.4$ kcal mol^{-1} [12].

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