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THE STANDARD FORMATION DATA FOR $KAlO_2$

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ABSTRACT

The standard enthalpy of formation of $KAlO_2$ was determined by hydrofluoric acid solution calorimetry to be $\Delta H^{\ominus}_{f,298.15} = -272.60 \pm 1.43$ kcal mol^{-1}. This value, combined with the previously determined low-temperature heat capacity and high-temperature enthalpy functions, provides the Gibbs energies and equilibrium constants of formation over the temperature range of the measurements. The standard Gibbs energy was determined as $\Delta G^{\ominus}_{f,298.15} = -257.45$ kcal mol^{-1}.

INTRODUCTION

Low-temperature heat capacity and high-temperature enthalpy data for $KalO_2$ have been published [1]. The enthalpy of formation for $KAlO_2$ as determined in this study completes the data for the alkali series. Data for aluminates of lithium, sodium, rubidium, and cesium have been published [2].

MATERIALS

Acids

The acids were reagent-grade products that were used without treatment except for dilution with distilled water to the proper concentration.

Potassium aluminate

The sample synthesized for a previous study [1] also was used for the measurements made in this work. This very hygroscopic material was handled in a dry box charged with specially desiccated CO_2 gas. It was loaded into preweighed, specially designed capsules, sealed, then reweighed and stored in a desiccator over newly calcined CaO before use.

TABLE 1

Reaction scheme for $KAlO_2(c)$ [a]

Reaction	$\Delta H^{\ominus}$ (kcal)	Uncertainty (kcal)
(1) $AlCl_3 \cdot 6H_2O(c) \rightarrow Al^{3+}(sol) + 3Cl^-(sol) + 6H_2O(sol)$	−19.183	±0.075
(2) $KCl(c) \rightarrow K^+(sol) + Cl^-(sol)$	+1.923	±0.005
(3) $46.924H_2O(l) \rightarrow 46.924H_2O(sol)$	+33.785	±0.047
(4) $4(HCl \cdot 12.731H_2O)(l) \rightarrow 4H^+(sol) + 4Cl^-(sol)$ $+ 50.924H_2O(sol)$	+41.508	±0.060
(5) $KAlO_2(c) + 4H^+(sol) \rightarrow K^+(sol) + Al^{3+}(sol)$ $+ 2H_2O(sol)$	−71.832	±0.189
$\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$		
(6) $KCl(c) + AlCl_3 \cdot 6H_2O(c) + 46.924H_2O(l)$ $\rightarrow KAlO_2(c) + 4(HCl \cdot 12.731H_2O)(l)$		
$\Delta H_6 = +46.849 \pm 0.217$ kcal		

For reactions (1)–(5), introduced reactants are at 25 ° C and reaction products are at 73.7 ° C.

Other components

The enthalpy of solution values for other compounds used in the reaction scheme (Table 1) were determined previously, and the data were adopted directly.

EXPERIMENTAL DETERMINATIONS

Enthalpies of solution at 298 K

The enthalpy of solution of potassium aluminate was determined by hydrofluoric acid solution calorimetry. The apparatus used was described by Torgeson and Sahama [3], with later modifications described by King [4]. Some more recent alterations are described by Bennington et al. [5].

The aqueous solution medium was 948.7 g of a mixture containing 20.0 wt% HF and 5.0 wt% HCl. The quantities of the reacting substances were calculated stoichiometrically with 1.000 g of $AlCl_3 \cdot 6H_2O$ substituted in reaction (1) of Table 1.

Weighed amounts of the substances to be dissolved were placed in a paraffin-sealed Teflon-tape * capsule and dropped at the appropriate time from room temperature into the calorimeter, which was operated at 73.7 ° C. Each measured heat effect resulted from a process of converting a pure substance at 25 ° C to a solution product at 73.7 ° C. Combination of the

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* Reference to specific products does not imply endorsement by the Bureau of Mines.

measurements in accordance with reaction schemes resulted in the evaluation of a standard enthalpy of reaction. Separate measurements provided corrections for the heat effects caused by the Teflon capsules and paraffin sealant. Electrical calibrations of the calorimeter were made over the temperature range of the measurements following each determination.

Throughout this report, uncertainties were assigned to measured heat and derived enthalpy values as follows: (i) when several individual heat values were measured for a reaction, the precision uncertainty was taken as $2\sqrt{\Sigma d_i^2/[n(n-1)]}$, where Σd_i^2 is the sum of the squares of the deviation from the mean value and n is the number of determinations; and (ii) when the heats of two or more reactions were combined, 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). All weights were corrected to vacuum, and 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].

The reaction scheme for the calorimetric investigation is presented in Table 1. The reactions are written in an abbreviated form, adequate to show that stoichiometry was maintained in such a way as to permit cancellation of appropriate reactants and products. Also included are the mean measured heat values and their precision uncertainties.

The enthalpy of solution and precision uncertainty for $KAlO_2$ was determined to be $\Delta H_{sol} = -71.832 \pm 0.189$ kcal mol^{-1}, which was the mean provided by seven measurements (−72.072, −71.569, −71.808, −72.099, −71.508, −71.830, and −71.936). The sample size used was stoichiometric with 0.004 mol $AlCl_3 \cdot 6H_2O$.

The final solution after conducting reactions (1), (2), and (3) in sequence 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 enthalpy of solution values were substituted into the reaction scheme and combined according to

$$\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$$

to obtain the enthalpy change for reaction (6), the overall calorimetric reaction.

Standard enthalpy of formation

The calculation of the standard enthalpy of formation for potassium aluminate requires additional data from the literature. All of the necessary

TABLE 2

Enthalpy of formation of $KAlO_2$

Reaction	$\Delta H^{\ominus}_{f,298.15}$ (kcal mol^{-1})	Uncertainty (kcal mol^{-1})
(7) $Al(c)+1.5Cl_2(g)+6H_2(g)+3O_2(g) \rightarrow AlCl_3 \cdot 6H_2O(c)$	−643.60	±0.21
(8) $K(c)+0.5Cl_2(g) \rightarrow KCl(c)$	−104.385	±0.06
(9) $H_2(g)+0.5O_2(g) \rightarrow H_2O(l)$	−68.315	±0.01
(10) $13.231H_2(g)+0.5Cl_2(g)+6.3655O_2(g) \rightarrow HCl \cdot 12.731H_2O(l)$	−908.538	±0.33
$\Delta H_{11} = \Delta H_6 + \Delta H_7 + \Delta H_8 + 46.924\Delta H_9 - 4\Delta H_{10}$		
(11) $K(c)+Al(c)+O_2(g) \rightarrow KAlO_2(c)$		
$\Delta H_{11} = \Delta H^{\ominus}_{f,298.15} = -272.597 \pm 1.434$ kcal mol^{-1}		

data for the elements and oxides are from Pankratz [9]. The data for $AlCl_3 \cdot 6H_2O$ are from Coughlin [10]; data for HCl are from Wagman et al. [11], with the uncertainty taken from the JANAF tables [12]; and data for H_2O and $HCl \cdot 12.731H_2O$ are from Wagman et al. [11].

TABLE 3

Standard formation data for $KAlO_2$: $K(c, l, g)+Al(c, l)+O_2(g) \rightarrow KAlO_2(c)$

T (K)	ΔH_f (kcal mol^{-1})	ΔG_f (kcal mol^{-1})	log K
298.15	−272.597	−257.454	188.716
300.00	−272.600	−257.360	187.484
336.35 [a]	−272.662	−255.510	166.020
336.35	−273.220	−255.510	166.020
400.00	−273.269	−252.154	137.769
500.00	−273.222	−246.877	107.909
600.00	−273.066	−241.620	88.009
700.00	−272.840	−236.395	73.805
800.00	−272.575	−231.209	63.162
810.00 [b]	−272.547	−230.692	62.243
810.00	−272.237	−230.692	62.243
900.00	−272.098	−226.084	54.900
933.61 [c]	−272.054	−224.366	52.521
933.61	−274.634	−224.366	52.521
1000.00	−274.525	−220.796	48.254
1043.70 [d]	−274.452	−218.449	45.742
1043.70	−293.490	−218.449	45.742
1100.00	−293.261	−214.407	42.598
1200.00	−292.837	−207.255	37.746
1300.00	−292.391	−200.142	33.646
1400.00	−291.926	−193.062	30.138

[a] Melting point of K. [b] First-order transition. [c] Melting point of Al. [d] Calculated boiling point to ideal monatomic gas K.

The standard enthalpy of formation for potassium aluminate was derived from these reactions and enthalpies according to the scheme

$$\Delta H_{11} = \Delta H_6 + \Delta H_7 + \Delta H_8 + 46.924\Delta H_9 - 4\Delta H_{10}$$

for which $\Delta H^{\ominus}_{f,298.15} = -272.597 \pm 1.434$ kcal mol^{-1} (Table 2).

RESULTS

The value for the standard enthalpy of formation is combined with the low-temperature and high-temperature thermodynamic properties from the literature [1] to provide the standard formation data according to the reaction

$$K(c, l, g) + Al(c, l) + O_2(g) = KAlO_2(c)$$

These data, the enthalpies of formation, the equilibrium constants of formation, and the Gibbs energies of formation are presented as a function of temperature in Table 3. Potassium aluminate is shown to be stable throughout the range of the measurements.

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