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## 1. Introduction

The thermodynamic properties ( $C_p^\circ$ ,  $\Phi^\circ = -(G^\circ - H^\circ(0))/T$ ,  $S^\circ$ ,  $H^\circ - H^\circ(0)$ ,  $\Delta_f H^\circ$ ,  $\Delta_f \Delta G^\circ$ ) of condensed and gaseous lithium, sodium, potassium, rubidium, and cesium hydroxides in standard states have been reevaluated. This activity was stimulated by the existence of new data since the time of publication of four critical reviews containing analogous information [82GUR/VEY], [82MED/BER], [82WAG/EVA], [85CHA/DAV].

The principal difficulty in providing reliable properties of the alkali metal hydroxides is the lack of precise experimental information on (1) the crystalline phase transition, (2) heat capacity data for the liquid state, (3) vibrational frequencies of monomeric and dimeric molecules of hydroxides, (4) structural parameters for the dimeric molecules and data for the more complex species, (5) the composition of the vapor over the crystal and liquid phases and (6) the enthalpies of formation for the gaseous molecules.

This situation arises from the high chemical activity of alkali metal hydroxides. At elevated temperatures, all of these substances interact with most container materials, including Pt and Au, resulting in difficulties during experimental studies. Special problems occur in determining phase transition temperatures and heat capacities of liquids as well as the vapor pressure over the melts. The hydroxides can be easily contaminated in an atmosphere containing even small amounts of water, oxygen or carbon dioxide. Thus, some data for the solid and liquid hydroxides (including temperatures and enthalpies of phase transitions and fusion) are not very accurate. In many cases, commercial materials were used for measurements without additional purification.

Currently, the data on the composition of the alkali metal hydroxide vapors are rather qualitative. In the vapor phase, both monomer (MOH) and dimer ( $\text{M}_2\text{O}_2\text{H}_2$ ) molecules are present. Some evidence was obtained (see [60BER/MES], [60SCH/POR]) that trimers also existed in the vapors of lithium and sodium hydroxides. The same situation might be present over the melts of other hydroxides at high temperatures. Very small amounts of positive and negative ions, such as  $\text{MOH}^+$ ,  $\text{M}_2\text{OH}^+$ ,  $\text{M}(\text{OH})_2^+$ ,  $\text{M}_3(\text{OH})_3^+$ , and  $\text{M}_2(\text{OH})_3^-$ , were observed over the hydroxide melts in equilibrium conditions using a mass-spectrometric technique [86KUD/BUT]. The partial pressure of these ions is 11–15 orders of

magnitude less than the partial pressure of MOH and no experimental data on their structure or other constants are available. Thus, these ions as well as trimers of alkali metal hydroxides will not be treated in this review.

This review is divided into parts: Part 1 is devoted to the compounds of Li and Na; whereas Part 2 will be devoted to the compounds of K, Rb, and Cs. The review for each compound contains a brief description of all experimental and theoretical studies of thermodynamic and molecular constants linked with the calculations of tables of thermodynamic properties. The technique used, the impurities in the samples studied, the results obtained and the accuracy of the data are discussed in these reviews. Unfortunately, the literature includes several reports which were not available to the authors. We assume that the absence of these sources does not influence the accuracy of the adopted values and the calculated thermodynamic tables. In all cases, special attention was devoted to estimating the uncertainties of adopted values and calculated thermodynamic properties. The selected constants and calculated properties are compared with similar quantities in earlier reviews [82WAG/EVA], [82MED/BER], [82GUR/VEY] and [85CHA/DAV]. Of course, some recommendations are tentative due to the lack of reliable information. Recommendations for future measurements are given in Section 5.

All crystalline hydroxides of the alkali metals except LiOH possess polymorphism (see Table 1-1). All hydroxides have several other modifications at high pressures.

General comments:

- (1) The units used throughout the text and tables are: temperature in K; enthalpy, Gibbs energy and enthalpy of formation in  $\text{kJ mol}^{-1}$ ; entropy, Gibbs energy function, and heat capacity in  $\text{J K}^{-1} \text{mol}^{-1}$ .
- (2) In general, the literature coverage extends from the end of the last century to 1994.
- (3) The temperature scale used for the recommended values is ITS-90. Many of the data known in the literature were obtained using earlier temperature scales. Often times the scale used is not mentioned in the papers, so it was necessary to guess the appropriate corrections. It should be noted that below  $T = 1000 \text{ K}$ , the corrections between all temperature scales are less than 1 K, while from 1000 K to 2000 K the corrections are always less than 2 K and are well within the uncertainty of the temperature measurements.
- (4) The following relative atomic masses are adopted (93IUP): O, 15.9994; Na, 22.989768; Cs, 132.90543; H, 1.00794; K, 39.0983; Li, 6.941; Rb, 85.4678.
- (5) In the Appendices for each hydroxide, the experimental values of enthalpy, heat capacity, and equilibrium constant obtained in the cited studies are given.
- (6) Tables of "Thermodynamic Properties at 0.1 MPa" are calculated, using thermal functions for reference substances Li(cr and liq and g), Na(cr and liq and g), K(cr and liq and g), Rb(cr and liq and g), Cs(cr and liq and g),  $\text{H}_2(\text{g})$ , and  $\text{O}_2(\text{g})$  from [82GUR/VEY]. The transition

TABLE 1-1. Crystal structure and lattice parameters of the alkali metal hydroxides.

Phase	Temperature interval stability (K)	Crystal system	Symmetry class	Space group	Lattice parameters (nm)	T(K)	Reference
LiOH	0–746	tetragonal	4/mmm	P4/nmm	a=3.549 c=4.334	...	[33ERN]
$\alpha$ -NaOH	0–514	rhombic	mmm	Cmcm	a=3.4013 b=3.3984 c=11.378	294	[85JAC/KOC]
$\beta$ -NaOH	514–568	monoclinic	2/m	P2 <sub>1</sub> /m	a=3.435 b=3.445 c=6.080 $\beta$ =109.9°	535	[82BLE/DAC]
$\gamma$ -NaOH	568–594	cubic	m3m	Fm3m	a=5.10	578	[82BLE/DAC]
$\alpha$ -KOH	0–226.7	monoclinic	2/m	P2 <sub>1</sub> /m	a=5.903 b=3.942 c=7.722 $\beta$ =110.36°	100	[87MAC/JAC]
$\beta$ -KOH	226.7–517	monoclinic	2/m	P2 <sub>1</sub> /m	a=3.9549 b=3.9975 c=5.7305 $\beta$ =103.81°	295	[87MAC/JAC]
$\gamma$ -KOH	517–679	cubic	m3m	Fm3m	a=5.752	533	[87MAC/JAC]
$\alpha$ -RbOH	0–265	orthorhombic	mm2	Cmc2 <sub>1</sub>	a=4.1244 b=11.176 c=4.2110	193	[87JAC/MAC2]
$\beta$ -RbOH	265–508	monoclinic	2/m	P2 <sub>1</sub> /m	a=4.1506 b=4.245 c=6.030 $\beta$ =104.53°	338	[87JAC/MAC2]
$\gamma$ -RbOH	508–655	cubic	m3m	Fm3m	a=6.0802	550	[87JAC/MAC2]
$\alpha$ -CsOH	0–234	orthorhombic	mmm	Pmnb	a=4.3280 b=4.4777 c=11.586	77	[87BAS/ELC]
$\beta$ -CsOH	234–498	orthorhombic	mmm	Bmmb	a=4.3577 b=4.5238 c=12.018	293	[87BAS/ELC]
$\gamma$ -CsOH	498–615.5	cubic	m3m	Fm3m	a=6.427	503	[87JAC/MAC]

from condensed to gaseous occurs for lithium at 1622 K ( $\Delta_s H(\text{Li}, 0 \text{ K}) = 157.735 \text{ kJ mol}^{-1}$ ), for sodium at 1172 K ( $\Delta_s H(\text{Na}, 0 \text{ K}) = 107.763 \text{ kJ mol}^{-1}$ ), for potassium at 1039 K ( $\Delta_s H(\text{K}, 0 \text{ K}) = 89.891 \text{ kJ mol}^{-1}$ ), for rubidium at 967 K ( $\Delta_s H(\text{Rb}, 0 \text{ K}) = 82.192 \text{ kJ mol}^{-1}$ ) and for cesium at 948 K ( $\Delta_s H(\text{Cs}, 0 \text{ K}) = 78.014 \text{ kJ mol}^{-1}$ ). The uncertainties of the standard enthalpy and Gibbs energy of formation are estimated using uncertainties in the thermal functions adopted in this work and in [82GUR/VEY].

- (7) The fundamental constants used in the statistical mechanical calculations are from the CODATA recommendations (88COH/TAY).

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## 2. Lithium Hydroxide

### 2.1. Lithium Hydroxide in Condensed Phases

The crystal structure of LiOH was determined in [33ERN], showing it to belong to the tetragonal crystal system, symmetry class 4/mmm, space group P4/nmm (see Table 1-1). Unlike crystalline hydroxides of other alkali metals, lithium hydroxide exhibits no known polymorphism. There are published data suggesting a polymorphic transition of LiOH at 670–686 K, as determined by DTA ([53KHI/KHI], [58RES/UNZ]). As was shown later ([61COH/MIC], [64PER/RES]), the thermal effects observed were related to the fusion point of the eutectic LiOH-Li<sub>2</sub>CO<sub>3</sub>.

LiOH, as well as all other hydroxides of alkali metals, is very active chemically and is able to react with water and CO<sub>2</sub> at ambient temperature. Molten LiOH at 800–1200 K interacts with almost all container materials, including Ag and Pt, with resultant difficulties during experimentation. The LiOH melt interacts to a lesser extent with Au and Cr-Ni alloys which were used as the container material in several works.

### 2.1.1. Heat Capacity and Enthalpy Measurements

#### Temperatures below 298.15 K

##### [50BAU/JOH]

Bauer *et al.* measured the heat capacity of LiOH from 15.91 to 302.85 K (41 data points) in an adiabatic vacuum calorimeter. The commercial sample of LiOH, obtained from the Metalloy Corporation of Minneapolis, was purified by recrystallization of LiOH·H<sub>2</sub>O from triple-distilled water. The monohydrate was then decomposed at 150 °C in a stream of CO<sub>2</sub>-free air. Spectrographic analysis showed that the purified LiOH contained 0.01% Si and less than 0.001% Mg, Fe, Al, Cu, Na, Ni, Ca. No correction was applied for these impurities. Titration with hydrochloric acid gave a purity of 99.9±0.2%.

The calorimeter used was described in [50JOH/KER]; its volume was 72 cm<sup>3</sup>. Measurements were made with 31.069 g of LiOH. Uncertainties (as reported by Bauer *et al.*) were 0.2% above 45 K and 0.5% at 20 K. The reported heat capacity values are listed in Table 2-1 and presented in Fig. 2-1. Extrapolation below 16 K using Θ<sub>D</sub> (285 K) resulted in S°(16 K)=0.117 J K<sup>-1</sup> mol<sup>-1</sup> and H°(16 K)-H°(0)=1.42 J mol<sup>-1</sup>.

#### Temperatures above 298.15 K

##### [54POW/BLA]

Powers and Blalock measured the enthalpy of solid and liquid LiOH by drop calorimetry at 397–1213 K (113 data points). No initial analysis of the sample was made. The authors assumed that the LiOH sample contained 0.13% Li<sub>2</sub>CO<sub>3</sub> as impurity, as did the samples of NaOH and KOH investigated in the same study. The capsule material was Inconel (an alloy of Ni-Cr-Fe). The final analysis showed 96.6% total alkalinity and 0.05% impurities. The measurements were made in a Bunsen ice calorimeter calibrated by use of an alumina standard. The determinations of the enthalpy of alumina (α-Al<sub>2</sub>O<sub>3</sub>) were within 3% of NBS results [47GIN/COR] (in the range 700–1200 K). The 48 measured enthalpy values for crystalline LiOH (397–737 K) and the 65 values for liquid LiOH (790–1213 K) are listed in Table 2-5 and shown in Figs. 2-2 and 2-3. The authors [54POW/BLA] did not estimate the accuracy of their measurements. The enthalpy values for LiOH(cr) and LiOH(liq) were represented by linear equations in the range 397–746 K (in cal g<sup>-1</sup>):

$$H^{\circ}(T) - H^{\circ}(273 \text{ K}) = -5 + 0.627(T - 273 \text{ K}),$$

and in the range 746–1213 K:

$$H^{\circ}(T) - H^{\circ}(273 \text{ K}) = 64 + 0.923(T - 273 \text{ K}).$$

The enthalpy of fusion at 746 K was recommended by [54POW/BLA] as 210 cal g<sup>-1</sup>=21.04 kJ mol<sup>-1</sup>.

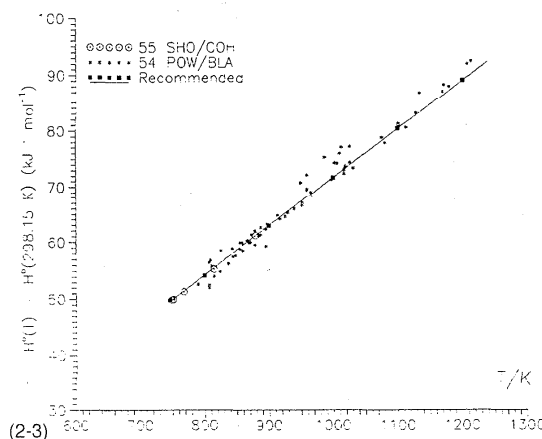
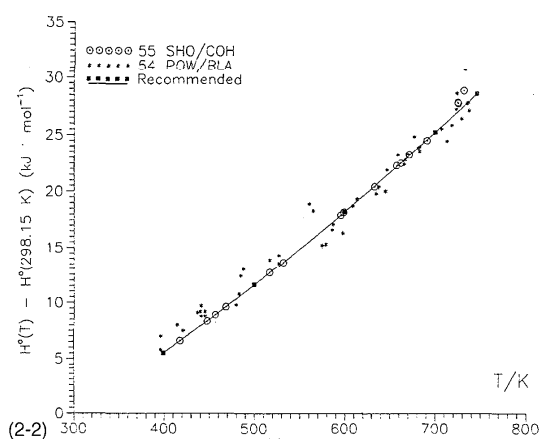
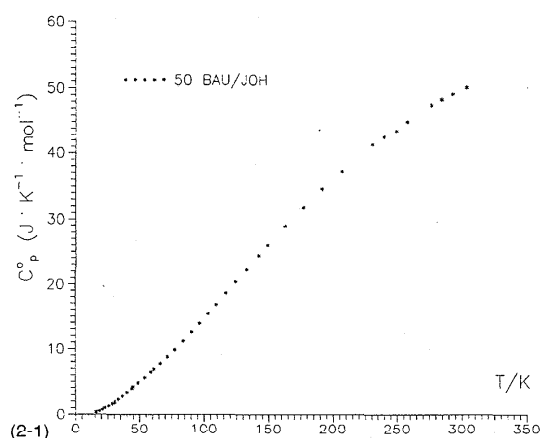


FIG. (2-1). Heat capacity of LiOH at 15–300 K.  
 (2-2) Enthalpy  $H^\circ(T) - H^\circ(298.15 \text{ K})$  for solid LiOH at 298.15–746 K.  
 (2-3) Enthalpy  $H^\circ(T) - H^\circ(298.15 \text{ K})$  for liquid LiOH at 746–1200 K.

#### [55SHO/COH]

Shomate and Cohen measured the enthalpy of crystalline and liquid LiOH by drop calorimeter at 418.3–878.6 K (21 data points). A sample of LiOH was prepared from carefully

purified lithium by solution in distilled water and decomposition of  $\text{LiOH} \cdot \text{H}_2\text{O}$  in a dry,  $\text{CO}_2$ -free helium stream at 350 °C. Analysis of the LiOH sample showed only traces of carbonate. No corrections were made for any impurities. The calorimeter used was described in [46KEL/NAY]. The container for the LiOH sample was made from gold. The calorimeter was calibrated by measurements of the enthalpy of alumina; the values obtained were slightly lower than those recommended by NBS [47GIN/COR]; the mean deviation at temperatures below 800 K was 0.1%. The reported 16 enthalpy values for solid LiOH (418.3–731.5 K) and 5 values for liquid LiOH (748.5–878.6 K) are listed in Table 2-3 and given in Figs. 2-2 and 2-3.

The results of this study can be considered as the most reliable at the present time: maximum deviation of the measured enthalpy values of solid LiOH from the equation in the range 418–690 K did not exceed 0.4%; average deviation is 0.15%. At higher temperatures the measured enthalpy values lie higher (by 2.5–4.8%) than the values calculated using the equation. This phenomenon may be due to premelting of the sample. Therefore these three points were not taken into account by [55SHO/COH] in the least-squares calculation of the equations for enthalpy and heat capacity of solid LiOH (in  $\text{cal mol}^{-1}$  and  $\text{cal K}^{-1} \text{ mol}^{-1}$ , respectively):

$$H^\circ(T) - H^\circ(298 \text{ K}) = 11.988 T + 4.12 \times 10^{-3} T^2 + 2.267 \times 10^5 T^{-1} - 4701;$$

$$C_p^\circ = 11.988 + 8.24 \times 10^{-3} T - 2.267 \times 10^5 T^{-2}.$$

For liquid LiOH (744.3–900 K) the following equations and values were calculated:

$$H^\circ(T) - H^\circ(298 \text{ K}) = 20.74 T - 3638 \text{ cal mol}^{-1},$$

$$C_p^\circ = 20.74 \text{ cal K}^{-1} \text{ mol}^{-1}$$

and

$$\Delta_{\text{fus}} H^\circ(744.3 \text{ K}) = 5.01 \text{ kcal mol}^{-1}.$$

#### [77TYE/DES]

Tye *et al.* measured several thermophysical properties of pure (“reagent”) LiOH and commercial (storage material) LiOH. The first sample was stated to be 99.8% LiOH with 0.1% impurities (no specific mention is made of  $\text{Li}_2\text{CO}_3$  and  $\text{H}_2\text{O}$  as impurities), whereas the second sample was 95% LiOH and 3%  $\text{Li}_2\text{CO}_3$ . The authors measured the heat capacity and enthalpy of both samples, but no primary values were given in the paper. Only the smoothed heat capacity values at 3 temperatures for the solid and at 2 temperatures for the liquid were reported:

#### Heat capacity of LiOH in $\text{J K}^{-1} \text{ mol}^{-1}$ [77TYE/DES]

T/K	573	673	713	825	873
LiOH, reagent	69.9	75.4	80.9	94.4	87.6
LiOH, commercial	65.4	73.0	76.4	99.4	90.8

Information on the accuracy of the measurements was not presented. It must be considered low because the samples were of unknown purity and the data for the two samples are contradictory: in the solid state, the heat capacity of the commercial LiOH was 3–6% smaller and in the liquid state 4–6% greater than that of the "reagent" sample. The enthalpies of fusion of these samples (26.6 and 24.3 kJ mol<sup>-1</sup>, respectively) are 20–30% higher than the results of more accurate measurements.

#### Discussion of Heat Capacity and Enthalpy Data

The measurements of the heat capacity at low temperatures (16–303 K) carried out by Bauer, Johnston and Kerr [50BAU/JOH] are the only available data at the present time (see Table 2-4 and Fig. 2-1). The authors estimated the uncertainties of these data below 45 K as 0.5% and above 45 K as 0.2% and the uncertainty of the selected value of entropy at 298.15 K as 0.20 J K<sup>-1</sup> mol<sup>-1</sup>. Extrapolation of the heat capacity below 16 K by a cubic law ( $\Theta_D=285$  K) yielded a small value  $S^\circ(16\text{ K})=0.117\text{ J K}^{-1}\text{ mol}^{-1}$ . The authors did not find any anomaly in the heat capacity behavior. The experimental heat capacity data [50BAU/JOH] are recalculated by the method [86IOR/TOL]. The results of this calculation are:

$$\begin{aligned} C_p^\circ(298.15\text{ K}) &= 49.58 \pm 0.20\text{ J K}^{-1}\text{ mol}^{-1}, \\ S^\circ(298.15\text{ K}) &= 42.81 \pm 0.20\text{ J K}^{-1}\text{ mol}^{-1}, \\ H^\circ(298.15\text{ K}) - H^\circ(0) &= 7414 \pm 30\text{ J mol}^{-1}. \end{aligned}$$

These values coincided satisfactorily with the values adopted by [50BAU/JOH]. The adopted values are compared with those recommended in selected other reviews in Table 2-4.

Figure 2-2 shows the enthalpy  $H^\circ(T) - H^\circ(298.15\text{ K})$  measured in [55SHO/COH] and [54POW/BLA]. These studies are not equivalent in reliability. The data of Shomate and Cohen [55SHO/COH] were obtained in a drop calorimeter calibrated by alumina standard with 0.2% accuracy. Thirteen enthalpy values for LiOH in the temperature interval from 418.3 K to 690.8 K were of high precision; they were fitted to an equation in which the heat capacity increases rapidly from  $C_p^\circ(298.15\text{ K})=49.58\text{ J K}^{-1}\text{ mol}^{-1}$  [50BAU/JOH] to 74.00 J K<sup>-1</sup> mol<sup>-1</sup> at the melting point 746 K. Note that [55SHO/COH] discarded three enthalpy points in the temperature interval from 724.6 to 731.5 K which were 2.5–4.8% greater than the values calculated by the equation. This phenomenon can be explained either by an anomalously rapid increase in the heat capacity near the melting point or as "premelting" which indicates that the amount of impurities was probably greater than was reported in [55SHO/COH]. Above the fusion point the authors could measure only 5 values of enthalpy in the narrow temperature interval from 748.5 to 878.6 K, as at higher temperatures the gold capsules corroded and the LiOH melt flowed out. The heat capacity of LiOH(liq) was determined as 87.3 J K<sup>-1</sup> mol<sup>-1</sup>.

The aim of the work of Powers and Blalock [54POW/BLA], using a Bunsen ice calorimeter, was to measure the enthalpy of LiOH to the highest possible temperatures. These

authors met serious difficulties concerning the interaction of LiOH melt with capsule material. The heat capacity of the thick-walled Inconel capsules approached 50% of the heat capacity of the system (capsule+sample) resulting in low accuracy measurements. Reproducibility of the measurements was low especially for LiOH(cr): the average deviation was 7% at 397–600 K and 3% at 600–737 K; while for LiOH(liq) the average deviation was 2% at 790–1213 K. The authors fitted their enthalpy data with linear equations; the derived constant heat capacity values were 63±4 J K<sup>-1</sup> mol<sup>-1</sup> for LiOH(cr) and 92±4 J K mol<sup>-1</sup> for LiOH(liq). Note that these measurements [54POW/BLA] appear to have systematic errors resulting in overestimation of the results. This conclusion follows from an examination of the enthalpy values of alumina used as a standard: the values from [54POW/BLA] at 773 K are 3.3% higher and at 1073 K are 2.4% higher than those recommended by NBS [47GIN/COR]. Similarly, in [54POW/BLA] the enthalpy values obtained for NaOH were greater in comparison to [54DOU/DEV].

The equation  $C_p=51.381+32.796\times 10^{-3}T-10.293\times 10^5T^{-2}\text{ J K}^{-1}\text{ mol}^{-1}$ , derived from the data of [55SHO/COH], is recommended for the heat capacity of LiOH(cr). Comparing the adopted values for LiOH(cr) with the heat capacity values at 573, 673 and 713 K, reported by Tye *et al.* [77TYE/DES], shows that the latter values are 4, 5, and 10% higher than the adopted ones. As has been discussed already, the data of this study which are not considered reliable are not taken into account.

In selecting the enthalpy and heat capacity values for LiOH(liq), the considerations already stated are followed. Analysis of the results of two investigations of enthalpy of liquid LiOH shows that the values from [54POW/BLA] lie about 1% higher than those from [55SHO/COH]. Taking into account the possible systematic errors in the data of [54POW/BLA] resulting in overestimation, the values given in [55SHO/COH] are preferred. The equations for the enthalpy increment and the heat capacity of LiOH(liq) are:

$$\begin{aligned} H^\circ(T) - H^\circ(298.15\text{ K}) &= 87.3 T - 15221\text{ J mol}^{-1}; \\ C_p &= 87.3\text{ J K}^{-1}\text{ mol}^{-1}, \end{aligned}$$

as derived from the data [55SHO/COH], 748.5–878.6 K, by the least-squares method. The heat capacity value, 87.3 J K<sup>-1</sup> mol<sup>-1</sup>, differs from the value, 86.8 J K<sup>-1</sup> mol<sup>-1</sup>, reported by [55SHO/COH], because the latter value was derived from only two experimental enthalpy values at 748.5 and 878.6 K. Note that the measurements of heat capacity of pure ("reagent") LiOH at 823 K and 873 K in [77TYE/DES] result in an improbably sharp decrease of heat capacity, apparently due to errors in the measurements.

#### Phase Equilibrium Data

It is well established that at ambient pressure LiOH(cr) has only one allotropic tetragonal modification. The published data on a polymorphic transition of LiOH at 670–686 K

[53KHI/KHI], [58RES/UNZ] were erroneous as they relate to the fusion point of the eutectic LiOH-Li<sub>2</sub>CO<sub>3</sub> [64PER/RES].

[15SCA]

Scarpa investigated the phase diagrams of the systems LiOH-LiF, LiOH-LiCl, LiOH-LiI and determined  $T_{\text{fus}} = 462^\circ\text{C} = 735\text{ K}$  for LiOH containing 0.8% Li<sub>2</sub>CO<sub>3</sub> and 0.7% H<sub>2</sub>O as impurities. This value is underestimated.

[51DIO], [52RES/DIO]

Diogenov [51DIO] studied the LiOH-LiNO<sub>3</sub> system and determined the melting point of LiOH by the visual method of thermal analysis as  $477^\circ\text{C} = 750\text{ K}$ . The same result was obtained by Reshetnikov and Diogenov [52RES/DIO] who studied the system LiOH-Li<sub>2</sub>CrO<sub>4</sub> by the same method. The samples were melted in a silver container in dry air free from CO<sub>2</sub>; the temperature was measured by a nichrome-constantan thermocouple immersed in the melt.

[53KHI/KHI]

Khitrov *et al.* determined the fusion temperature of LiOH as  $462^\circ\text{C} = 735\text{ K}$  by differential thermal analysis (DTA). The thermal anomaly at  $413^\circ\text{C} = 686\text{ K}$ , related to the fusion point of eutectic LiOH-Li<sub>2</sub>CO<sub>3</sub>, was observed in this study. The sample evidently contained significant Li<sub>2</sub>CO<sub>3</sub> impurity.

[54POW/BLA]

Powers and Blalock studying the enthalpy of LiOH determined the enthalpy of fusion of LiOH (at 746 K) as  $210\text{ cal g}^{-1} = 21.4\text{ kJ mol}^{-1}$  (see the discussion of the enthalpy data).

[55SHO/COH]

Shomate and Cohen determined the fusion temperature of LiOH in a separate experiment. The gold capsule with LiOH was placed in a furnace whose temperature was slightly greater than  $T_{\text{fus}}$ . Six hours were required to melt the sample. LiOH exhibited a sharp fusion at 744.3 K. Although the authors believed that LiOH contained only traces of Li<sub>2</sub>CO<sub>3</sub>, premelting of the sample was observed in the range 724–732 K (see above), showing that the sample was probably not as pure as thought.

The authors [55SHO/COH] determined the enthalpy of fusion as  $5.01\text{ kcal mol}^{-1} = 20.96\text{ kJ mol}^{-1}$  from the equations for enthalpy of crystal and liquid LiOH. These measurements are the most precise in the available literature.

[58RES/UNZ], [59RES/UNZ]

Reshetnikov and Unzhakov studied the system LiOH-LiCl and determined the fusion temperature of LiOH by two methods: DTA ( $470^\circ\text{C} = 743\text{ K}$ ) and the visual method of thermal analysis ( $477^\circ\text{C} = 750\text{ K}$ ). These values cannot be considered reliable because of the absence of chemical analysis of the LiOH sample. In addition, the authors [59RES/UNZ] found the thermal effect at 670–683 K related to the melting point of the eutectic LiOH-Li<sub>2</sub>CO<sub>3</sub>, indicating sample impurity problems.

[59ROL/COH]

Rollet *et al.* determined the fusion temperature of LiOH as  $473.0 \pm 0.3^\circ\text{C} = 746.15\text{ K}$  by a thermal analysis method.

LiOH was prepared by electrolysis of water solution of Li<sub>2</sub>CO<sub>3</sub> in a stream of hydrogen, then purified from CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, and ClO<sub>3</sub><sup>-</sup> ions and dehydrated until a constant fusion temperature was reached. The samples were melted in platinum ampoules; the temperature was measured by the copper-constantan thermocouple that was calibrated by  $T_{\text{fus}}$  of Zn (419.45 K; according to ITS-90, 419.58 K). The fusion temperature was measured with an uncertainty of 0.3°C.

[61COH/MIC], [67MIC], [68MIC]

Michaud and co-authors studied the phase diagrams of the systems LiOH-Li<sub>2</sub>CO<sub>3</sub> and LiOH-KOH. They prepared a LiOH sample according to the method described in the previous study [59ROL/COH] and confirmed the value  $473^\circ\text{C} = 746\text{ K}$  for the melting point of LiOH.

[64PER/RES]

Perfil'eva and Reshetnikov studied the system LiOH-Li<sub>2</sub>CO<sub>3</sub> and determined the fusion temperature of LiOH as  $475^\circ\text{C} = 748\text{ K}$  (DTA) and  $477^\circ\text{C} = 750\text{ K}$  (visual method of thermal analysis). The authors believed that the LiOH sample had 0.2% Li<sub>2</sub>CO<sub>3</sub> impurity.

[67RES/BAR], [69RES/BAR]

Reshetnikov and Baranskaya measured the fusion temperature and enthalpy of melting of LiOH. The fusion temperature was determined by DTA ( $474 \pm 1^\circ\text{C} = 747\text{ K}$ ) and by the visual method of thermal analysis ( $477 \pm 1^\circ\text{C} = 750\text{ K}$ ). The enthalpy of melting was determined by quantitative differential thermal analysis. The authors compared areas under the DTA curves corresponding to LiOH and using NaOH as a standard (enthalpy of melting for NaOH was adopted as equal to  $1.575\text{ kcal mol}^{-1}$ ). The accuracy of such a determination was estimated to be 10%. The value  $5.29\text{ kcal mol}^{-1} = 22.1\text{ kJ mol}^{-1}$  obtained for melting enthalpy cannot be considered as accurate, but it agrees with the more precise measurements of [55SHO/COH], [54POW/BLA] in the limits of inaccuracy indicated.

[69OST/ITK], [74POR/ITK]

Ostrovityanova and Itkina as well as Portnova and Itkina studied the systems LiOH-RbOH and LiOH-CsOH. They estimated that the LiOH samples contained less than 0.4% impurities. Determination of the melting point was carried out in a gold container by DTA and gave the values  $475^\circ\text{C} = 748\text{ K}$  in the first study and  $470\text{--}475^\circ\text{C}$  (743–748 K) in the second study. Heating curves were analyzed. Because the rate of heating was so high according to the thermograms presented ( $10\text{ deg min}^{-1}$ ), the reliability of  $T_{\text{fus}}$  values is rather low.

[71ADO], [71MIC/ERB]

The system LiOH-Ba(OH)<sub>2</sub> was investigated in these studies. A commercial LiOH sample ("Merck") was dehydrated at 200–400°C for 20 hours in dry nitrogen, free from CO<sub>2</sub>. The fusion temperature of LiOH,  $T_{\text{fus}} = 473^\circ\text{C} = 746\text{ K}$ , was measured by DTA (cooling curves were analyzed). The enthalpy of fusion of LiOH was calculated,  $\Delta_{\text{fus}}H = 4.85\text{ kcal mol}^{-1} = 20.3\text{ kJ mol}^{-1}$ , based on the phase dia-



gram for the system LiOH-Ba(OH)<sub>2</sub>. The reliability of this value was not evaluated.

[77TYE/DES]

Tye *et al.* determined the enthalpy of fusion for commercial LiOH ("pure reagent") as 24.3 kJ mol<sup>-1</sup> by means of calorimetric method (see earlier discussion of this work). This value is 15% higher than the most precise value 20.9 kJ mol<sup>-1</sup> [55SHO/COH]. Unfortunately, the primary numbers and data concerning accuracy of the measurements were not presented in the article. These measurements are considered to have low reliability.

[84TET/JOH]

Tetenbaum and Johnson measured the pressure of dissociation and calculated the enthalpy of dissociation for crystal and liquid LiOH. By subtraction of these values the authors calculated enthalpy of fusion as 22.6±1.7 kJ mol<sup>-1</sup>. This value cannot be considered as accurate, but it is in reasonable agreement with the more accurate value of 20.9±0.5 kJ mol<sup>-1</sup> [55SHO/COH].

#### Discussion of Phase Equilibrium Data

The results of measurements of the temperatures of fusion are shown in Table 2-5. Relatively old studies [15SCA] and [53KHI/KHI] gave underestimated values of the melting point. In other studies the values are scattered from 743 to 750 K. Several studies are considered to be less reliable because of poor characterization of the LiOH samples, in particular concerning the Li<sub>2</sub>CO<sub>3</sub> impurities. Studies of the system LiOH-Li<sub>2</sub>CO<sub>3</sub> in [61COH/MIC] and [64PER/RES] have shown that 1% Li<sub>2</sub>CO<sub>3</sub> contamination results in only a 2 K decrease of LiOH fusion temperature. Analysis of errors during measurements of fusion temperatures is of importance. Several studies have shown that routine DTA resulted in 2–3 K underestimated values of  $T_{\text{fus}}$ . Visual polythermal analysis (observation of crystal appearance upon slow decrease of the melt temperature) gives more reliable values.

The adopted fusion temperature,  $T_{\text{fus}} = 746 \pm 2$  K, is based on the most reliable results:

744.3 K—from the thermal analysis data [55SHO/COH],  
746 K—from the DTA data of [59ROH/COH, 61COH/MIC, 68MIC, 71MIC/ERB].

The uncertainty of the adopted values  $T_{\text{fus}}$  (±2 K) was estimated as it is impossible to evaluate the accuracy of the data tested in different studies (see Table 2-5).

The experimental values for enthalpy of fusion are shown in Table 2-6. The adopted value 20.9±0.5 kJ mol<sup>-1</sup> is based on the most reliable calorimetric measurements of enthalpy [55SHO/COH] taking into account the adopted equations for enthalpy of crystal and liquid LiOH. It is in good agreement with the value presented in the less precise study [54POW/BLA]. The values from other studies are considered to be less accurate.

#### Calculation of Thermal Functions of LiOH(cr and liq)

The thermal functions of LiOH(cr) for the temperatures 15–298.15 K (Table 2-7) are calculated using the data [50BAU/JOH] and spline technique [86IOR/TOL].

The following values are adopted:

$$C_p^\circ(298.15 \text{ K}) = 49.58 \pm 0.20 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$S^\circ(298.15 \text{ K}) = 42.81 \pm 0.20 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$H^\circ(298.15 \text{ K}) - H^\circ(0) = 7414 \pm 30 \text{ J mol}^{-1}.$$

The thermal functions of LiOH(cr and liq) for the temperatures 0–2000 K (Table 2-12) are calculated using these adopted values and the following (as presented in previous sections), and the data from Table 2-7. Heat capacity equation for the range 298.15–746 K:

$$C_p^\circ / \text{J K}^{-1} \text{ mol}^{-1} = 51.385 + 32.787 \times 10^{-3} T - 10.295 \times 10^5 T^{-2}.$$

$$\text{Temperature of fusion: } T_{\text{fus}} / \text{K} = 746 \pm 2$$

$$\text{Enthalpy of fusion: } \Delta_{\text{fus}} H / \text{J mol}^{-1} = 20900 \pm 500$$

Heat capacity value for range 746–2000 K:

$$C_p^\circ / \text{J K}^{-1} \text{ mol}^{-1} = 87.3$$

The uncertainties of the tabulated thermal functions at 298.15, 1000, and 2000 K are presented in Table 2-12. The calculated values of thermal functions of LiOH(cr and liq) are close to those listed in the reference books [82GUR/VEY] and [85CHA/DAV] (see Table 2-8).

#### 2.1.2. Enthalpy of Formation of LiOH(cr)

Two methods have been used for the determination of the enthalpy of formation of LiOH(cr): (1) calorimetric measurements of the enthalpy of solution of LiOH(cr) in water [the results of such studies are presented in the Table 2-9] and (2) equilibrium constant measurements for the reaction of decomposition  $2\text{LiOH}(\text{cr}) = \text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g})$ . The available data are given in Table 2-10. In reviewed studies, it was assumed that the activities of Li<sub>2</sub>O and LiOH remained close to unity.

#### Calorimetric Measurements

[1884TRU]

Truchot measured the enthalpy of solution of LiOH(cr) in water. No information about the LiOH sample, experimental techniques and the concentration of a final LiOH solution was given in the paper. This study cannot be considered as reliable.

[06FOR]

Forcrand carried out one measurement of the enthalpy of solution of LiOH(cr) at 297.15 K. His result cannot be considered as reliable, because the details on the experimental conditions (precision of temperature measurements, the method of analysis of final solution and so on) are missing.

[33UED]

Ueda measured the enthalpy of solution of LiOH(cr) in water in an isoperibol calorimeter at 298.15 K. The LiOH sample was not analyzed. The temperature was recorded on a Beckmann thermometer with precision of  $\pm 0.01^\circ$ . The heat exchange correction for the temperature rise in the calorimeter was not taken into account. Therefore it is difficult to assess the reliability of the Ueda data.

[61RES]

Reshetnikov measured the enthalpy of solution of LiOH(cr) in water in a isoperibol calorimeter at 298.15 K. The temperature was recorded on a platinum resistance thermometer with the precision of  $\pm 0.0005$  K. The energy equivalent of the calorimeter was determined by an electrical method. The calorimeter was calibrated by measuring the enthalpy of solution of KCl ( $\Delta_{\text{aq}}H^\circ(\text{KCl,cr} \rightarrow 400 \text{ H}_2\text{O}, 298.15 \text{ K}) = 17548 \pm 13 \text{ J mol}^{-1}$ ). The result obtained was in excellent agreement with the best literature data ( $17531 \pm 15 \text{ J mol}^{-1}$ ) [82MED/BER]. The author declared that the LiOH sample was pure, but did not quantitatively specify its purity. All preparative handling as well as the loading of the calorimeter sample holder was made in a nitrogen filled glove box.

[89KON/COR2]

Konings *et al.* measured the enthalpy of solution of LiOH(cr) in water in a precise isoperibol calorimeter at 298.15 K. The energy equivalent of the calorimeter was determined by an electrical method. The precision of temperature measurements was  $\pm 0.0002$  K. The LiOH sample had a high purity. No  $\text{Li}_2\text{CO}_3$  impurity was detected (titration with  $\text{HCl}(\text{aq})$ ). The Li content in the sample was found to be  $29.025 \pm 0.040$  mass percent (the calculated value is 28.983 mass percent). Lithium was analyzed, after dissolving the sample in  $\text{HCl}(\text{aq})$  and evaporating to dryness, by titration with silver nitrate. Assuming all excess lithium to be present as the oxide, the authors declared that the sample consisted of 99.71% LiOH and 0.29%  $\text{Li}_2\text{O}$ . The presence of  $\text{Li}_2\text{O}$  impurity was confirmed by x-ray powder-diffraction analysis and was taken into account in the calculations.

#### Studies of Equilibrium

[08JOH]

Johnston measured the dissociation pressure of LiOH(liq) by a static method for temperatures between 793 K and 1176 K using a mercury gauge. Data on the purity of the sample were not stated.

[53DIT/JOH]

The dissociation pressure of LiOH was measured by the Knudsen effusion method for temperatures between 648 K and 795 K. The study was made using a nickel Knudsen cell. The runs were made on material which was approximately 99.9% pure. A preliminary degassing run was made to ensure decomposition of any  $\text{LiOH} \cdot \text{H}_2\text{O}$ -impurity. The empirical equation  $\log p(\text{H}_2\text{O})/\text{atm} = (-7635.1 \text{ T}^{-1}) + 5.6786$  was derived to fit the experimental data. The authors [53DIT/

JOH] declared that the standard deviation of the experimental values of  $\log p(\text{H}_2\text{O})$  should be 0.02 (from all known sources of errors). Such a low error is unlikely for Knudsen effusion measurements. The observed standard deviation from the least squares curve was 0.14.

[55GRE/MOH]

Equilibrium pressures of  $\text{H}_2\text{O}$  vapor above LiOH and  $\text{Li}_2\text{O}$  were measured between 250 and  $400^\circ\text{C}$  by both transpiration (the carrier gas was nitrogen) and effusion methods. Two samples of LiOH were used. The first sample had a purity of 99.7%. The second sample contained 3.25%  $\text{Li}_2\text{O}$  as impurity. Two effusion cells were used (one of Monel and one of nickel). The authors [55GRE/MOH] assumed that the results from cell 2 should be discarded because the true equilibrium was not established in these experiments. The transpiration data were presented in a graphic ( $\log p(\text{H}_2\text{O}) \text{ T}^{-1}$ ) form only. Effusion results from cell 1 (17 points) agreed with those of the transpiration studies (24 points) and were assumed to represent equilibrium values. Both sets of data can be fitted well by the equation  $\log p(\text{H}_2\text{O})/\text{atm} = -7073 \text{ T}^{-1} + 2.102 \log T - 2.54 \times 10^{-3} \text{ T} + 2.767$ . The average deviation of the experimental  $\log p(\text{H}_2\text{O})$  values from the calculated values do not exceed 0.8%.

[60BER/MES]

The decomposition pressure of LiOH was studied by the mass-spectrometric/effusion technique in the temperature range 490–610 K. The results were presented in graphic form only. A platinum Knudsen cell with a 1 mm orifice was used. The reaction investigated was  $2^6\text{LiOD}(\text{cr}) = ^6\text{Li}_2\text{O}(\text{cr}) + \text{D}_2\text{O}(\text{g})$ . It was assumed that the difference between the energy of reactions for hydrogen- and deuterium-bearing molecules is negligible.

[84TET/JOH]

The partial pressure of  $\text{H}_2\text{O}(\text{g})$  above the  $\text{Li}_2\text{O}(\text{cr})$ -LiOH(cr,liq) system was determined for temperatures between 573 and 890 K. The partial pressures were measured by a transpiration method with continuous monitoring of the concentration of water vapour in a helium carrier gas. The reactor was made from platinum. A least squares analysis of the data below the point of fusion of LiOH (25 points) yielded the following equation for equilibrium pressures of  $\text{H}_2\text{O}$ :  $\log p(\text{H}_2\text{O})/\text{atm} = -(6718 \pm 140) \text{ T}^{-1} + (6.45 \pm 0.22)$ . The same analysis of data above the point of fusion of LiOH (8 points) yielded the equation  $\log p(\text{H}_2\text{O})/\text{atm} = -(4406 \pm 73) \text{ T}^{-1} + (3.27 \pm 0.09)$ . The errors are standard deviations. Third law enthalpies of the corresponding reactions were calculated from these measurements. Based on these measurements the enthalpy of fusion of LiOH was calculated to be  $\Delta_{\text{fus}}H^\circ(\text{LiOH,cr}) = 22.6 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1}$  (see Table 2-6).

[89MUN/NIS]

Munakata *et al.* measured the equilibrium decomposition pressure of LiOH(cr and liq) by the transpiration method in the temperature range 620–1020 K. The LiOH sample was placed in a reactor tube made from quartz or stainless steel.

Argon was used as the carrier gas. The water concentration was measured with a hygrometer. All experimental points, presented in a graphical form only, were fitted by two equations:

$$\log p(\text{H}_2\text{O})/\text{atm} = -5558.0 T^{-1} + 4.8198$$

for LiOH(cr) (620–744 K)

and

$$\log p(\text{H}_2\text{O})/\text{atm} = -4385.6 T^{-1} + 3.2870$$

for LiOH(liq) (744–1020 K).

These dissociation pressures were almost coincidental with those measured by Tetenbaum and Johnson [84TET/JOH] and by Gregory and Mohr [55GRE/MOH].

[91TER/MOH]

The equilibrium water vapour pressures above the Li<sub>2</sub>O–LiOH system were measured by a transpiration method over the range from 570 to 820 K. Two samples of LiOH were used (99.7% purity). Additional purification of samples was carried out by heating in vacuum at 700 °C. Nitrogen was used as a carrier gas. An optical hygrometer was used to measure continuously the moisture content of this gas. The uncertainties in the measurements of the temperature and pressure were estimated to be within ±2 K and ±2%. The equilibrium water vapour pressure is expressed by the following equations:

$$\log p(\text{H}_2\text{O})/\text{Pa} = (-4074 T^{-1} + 8.021) \pm 0.006;$$

above fusion point of LiOH,

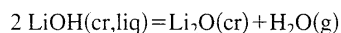
$$\log p(\text{H}_2\text{O})/\text{Pa} = (-6462 T^{-1} + 11.22) \pm 0.008;$$

below fusion point of LiOH.

The errors are standard deviations.

The  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  values for the decomposition reaction of LiOH (cr and liq) were determined to be  $123.7 \pm 0.18$  kJ mol<sup>-1</sup> and  $118.40 \pm 0.16$  J K<sup>-1</sup> mol<sup>-1</sup> at 601–740 K and  $78.00 \pm 0.10$  kJ mol<sup>-1</sup> and  $52.72 \pm 0.12$  J K<sup>-1</sup> mol<sup>-1</sup> at 749–820 K, respectively. The enthalpy and entropy of fusion of LiOH were calculated to be  $22.8 \pm 0.4$  kJ mol<sup>-1</sup> and  $30.34 \pm 0.28$  J K<sup>-1</sup> mol<sup>-1</sup>, respectively. In this paper the value  $\Delta_{\text{fus}} H^\circ(298.15 \text{ K}) = 20.9 \pm 0.5$  kJ mol<sup>-1</sup> was adopted.

The experimental data on the equilibrium constants at different temperatures for the reaction



obtained in works listed above are given in Table 2-11.

#### Discussion of the Enthalpy of Formation Data

The Truchot [1884TRU] and de Forcrand [06FOR] measurements have only a historical interest because at that time

experimental techniques, methods and materials were of a poor quality. Data of Ueda [33UED] cannot be considered reliable due to the inaccurate determination of the temperature rise in the calorimeter and the use of a sample that was not analyzed.

In the calorimetric investigations (Table 2-9), the study of Konings *et al.* [89KON/COR2] is the most accurate. This work was carried out more carefully than others. The authors used a precise technique and their lithium hydroxide sample was of known purity. Corrections were made for the observed impurities. LiOH(cr) can contain a Li<sub>2</sub>O-impurity, which easily reacts with atmospheric CO<sub>2</sub> and water. Thus extreme precautions must be taken during the preparation and storage of the LiOH samples. Apparently, such precautions were taken into account only by authors of [89KON/COR2].

The Konings *et al.* value for the enthalpy of solution of LiOH(cr) in water ( $-21.03 \pm 0.06$  kJ mol<sup>-1</sup>) is about 2.5 kJ mol<sup>-1</sup> less negative than the value of Reshetnikov [61RES], from which the authors of the JANAF Tables [85CHA/DAV] as well as Gurvich *et al.* [82GUR/VEY] derived the enthalpy of formation of LiOH(cr). Since Reshetnikov did not quantitatively specify the purity of his LiOH sample, his data are less reliable. In view of the experimental difficulties to avoid lithium-oxide impurities in lithium hydroxide, it is possible that the cause of difference in  $\Delta_f H$  values is traceable to the initial sample compositions. It can be also due to a possible presence of Li<sub>2</sub>CO<sub>3</sub> impurity in the Reshetnikov sample. Supportive evidence for a lower reliability of the  $\Delta_f H^\circ(\text{LiOH}, \text{cr}, 298.15 \text{ K})$  value based on the Reshetnikov result is found in dissociation pressure measurements (see Table 2-10).

The results by Ditmars and Johnson [53DIT/JOH] are evidently in error since no change in slope was observed near the melting point of LiOH. The LiOH dissociation pressure measurements below 744 K reported by Gregory and Mohr [55GRE/MOH], Tetenbaum and Johnson [84TET/JOH], Munakata *et al.* [89MUN/NIS] and Terai *et al.* [91TER/MOH] are in good agreement. The  $\Delta_r H^\circ(\text{LiOH}, \text{cr}, 298.15 \text{ K})$  values (third law) based on these measurements are in excellent agreement with the calorimetric value obtained by Konings *et al.* [89KON/COR2]. The LiOH dissociation pressure measurements of these authors above the fusion point of lithium hydroxide are in agreement with the values of  $\Delta_r H^\circ(\text{LiOH}, \text{cr}, 298.15 \text{ K})$ . Nevertheless, the calorimetric value [89KON/COR2] can be considered as more reliable, because the absence of precise knowledge of Li<sub>2</sub>O and LiOH activities can be a source of systematic errors. This problem is partially discussed in the works [84NOR/HIG], [85TET/FIS] and [91TER/MOH].

Data on the dissociation pressure of LiOH obtained in the works [08JOH] and [60BER/MES] lead to somewhat less reliable values of  $\Delta_r H^\circ(\text{LiOH}, \text{cr}, 298.15 \text{ K})$ . Other measurements of the dissociation pressures of LiOH(cr) were reported in the Terai *et al.* study [91TER/MOH]; Yoshida *et al.* [82YOS/KON] (670–740 K) (the article was not accessible to us); and unpublished work of Takeshita and Wa-

tanabe [91TAK/WAT] (550–690 K) (the data agree fairly well with the [91TER/MOH] results). Details of these latter measurements are unknown.

Thus we recommend for the enthalpy of formation of LiOH(cr) the value

$$\Delta_f H^\circ(\text{LiOH,cr,298.15 K}) = -487.5 \pm 0.1 \text{ kJ mol}^{-1}$$

based on the study by Konings *et al.* [89KON/COR2].

The adopted value of  $\Delta_f H^\circ(\text{LiOH,cr,298.15 K})$  and the values recommended in the major critical reviews are compared in Table 2-4.

### 2.1.3. Appendix. Tables of Experimental and Evaluated Data

TABLE 2-1. Experimental heat capacity values of LiOH [50BAU/JOH].

N	T K	$C_p^\circ$	
		cal K <sup>-1</sup> mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>
1	15.91	0.090	0.377
2	18.66	0.131	0.548
3	20.89	0.181	0.757
4	22.97	0.244	1.021
5	25.82	0.315	1.318
6	28.86	0.396	1.657
7	30.71	0.457	1.912
8	33.39	0.554	2.318
9	36.55	0.667	2.791
10	40.06	0.798	3.339
11	44.04	0.938	3.925
12	44.75	1.000	4.184
13	48.95	1.142	4.778
14	54.20	1.335	5.586
15	58.94	1.550	6.485
16	61.10	1.654	6.920
17	66.23	1.856	7.766
18	71.92	2.098	8.778
19	77.62	2.360	9.874
20	84.08	2.677	11.201
21	90.52	3.000	12.552
22	96.76	3.322	13.899
23	103.34	3.68	15.406
24	109.49	4.01	16.795
25	116.96	4.44	18.602
26	124.56	4.88	20.431
27	132.86	5.328	22.292
28	141.97	5.829	24.389
29	149.04	6.216	26.008
30	162.75	6.904	28.886
31	177.01	7.592	31.765
32	191.45	8.257	34.547
33	206.75	8.872	37.120
34	230.43	9.857	41.242
35	239.44	10.137	42.413
36	248.88	10.398	43.505
37	257.38	10.733	44.907
38	275.93	11.316	47.346
39	283.83	11.526	48.225
40	292.32	11.725	49.057
41	302.85	11.956	50.024

TABLE 2-2. Experimental enthalpy values  $H^\circ(T) - H^\circ(273.15 \text{ K})$  of LiOH [54POW/BLA].

N	T K	$H^\circ(T) - H^\circ(273.15 \text{ K})$	
		cal g <sup>-1</sup>	J mol <sup>-1</sup>
1	397	82	8216
2	397	70	7014
3	415	92	9218
4	422	87	8717
5	437	103	10320
6	440	104	10420
7	441	109	10920
8	441	100	10020
9	445	104	10420
10	445	100	10020
11	480	110	11020
12	483	120	12020
13	485	136	13620
14	488	142	14220
15	517	151	15130
16	527	148	14820
17	527	155	15530
18	561	201	20140
19	565	195	19530
20	575	164	16430
21	579	165	16530
22	586	178	17830
23	587	183	18330
24	598	175	17530
25	609	199	19930
26	614	205	20540
27	635	210	21040
28	638	216	21640
29	645	212	21240
30	647	231	23140
31	659	244	24440
32	666	236	23640
33	667	240	24040
34	669	245	24540
35	677	260	26050
36	681	250	25050
37	683	251	25150
38	683	247	24740
39	707	267	26750
40	713	256	25650
41	718	270	27050
42	723	284	28450
43	724	298	29850
44	729	276	27650
45	733	319	31960
46	735	289	28950
47	736	290	29050
48	737(cr)	283	28350
49	790(liq)	537	53800
50	807	576	57710
51	807	532	53300
52	807	537	53800
53	809	580	58110
54	811	570	57110
55	815	552	55310
56	824	560	56110

TABLE 2-2. Continued.

N	T K	$H^\circ(T) - H^\circ(273.15 \text{ K})$	
		cal g <sup>-1</sup>	J mol <sup>-1</sup>
57	825	596	59710
58	837	574	57510
59	843	599	60010
60	844	586	58710
61	848	588	58910
62	855	610	61120
63	855	599	60010
64	858	610	61120
65	859	596	59710
66	866	614	61520
67	869	610	61120
68	871	611	61220
69	873	624	62520
70	878	631	63220
71	878	606	60720
72	884	623	62420
73	887	624	62520
74	887	637	63820
75	895	634	63520
76	895	604	60520
77	897	643	64420
78	913	659	66030
79	917	653	65430
80	925	657	65830
81	929	664	66530
82	939	671	67230
83	949	719	72040
84	951	682	68330
85	951	677	67830
86	959	733	73440
87	959	707	70840
88	965	702	70340
89	967	694	69530
90	987	764	76550
91	997	724	72540
92	1002	754	75550
93	1006	753	75450
94	1010	771	77250
95	1013	782	78350
96	1017	742	74340
97	1017	735	73640
98	1019	748	74940
99	1026	783	78450
100	1026	755	75650
101	1031	745	74640
102	1075	799	80050
103	1080	790	79150
104	1101	823	82460
105	1101	818	81960
106	1113	816	81760
107	1127	842	84360
108	1133	879	88070
109	1169	881	88270
110	1171	893	89470
111	1179	890	89170
112	1207	930	93180
113	1213	935	93680

TABLE 2-3. Experimental enthalpy values  $H^\circ(T) - H^\circ(298.15 \text{ K})$  of LiOH [55SHO/COH]; (p)=premelting.

N	T K	$H^\circ(T) - H^\circ(298.15 \text{ K})$	
		cal mol <sup>-1</sup>	J mol <sup>-1</sup>
1	418.3	1577	6598
2	447.3	1991	8330
3	456.5	2128	8904
4	468.2	2297	9611
5	516.8	3032	12686
6	532.0	3272	13690
7	595.6	4281	17912
8	599.0	4345	18179
9	633.2	4883	20430
10	657.5	5330	22301
11	662.1	5383	22522
12	671.3	5556	23246
13	690.8	5855	24497
14	724.6(p)	6652	27832
15	725.1(p)	6632	27748
16	731.5(p)(cr)	6900	28870
17	748.5(liq)	11914	49848
18	751.2	11930	49915
19	767.5	12264	51313
20	814.3	13222	55321
21	878.6	14612	61137

TABLE 2-4. Comparison of the heat capacity, enthalpy, entropy, and enthalpy of formation values for LiOH (cr).

Reference	$C_p^\circ$ (298.15 K)	$S^\circ$ (298.15 K)	$H^\circ(298.15 \text{ K})$ $-H^\circ(0)$	$\Delta_f H^\circ$ (298.15 K)
	J K <sup>-1</sup> mol <sup>-1</sup>		J mol <sup>-1</sup>	kJ mol <sup>-1</sup>
82MED/BER	49.58±0.20	42.80±0.20	7414±40	-484.93±0.25
82WAG/EVA	49.66	42.80	7414	-484.93±0.25
82GUR/VEY	49.58	42.76±0.4	7406±40	-484.90±0.25
85CHA/DAV	49.591	42.821±0.21	7416	-484.93±0.4
89KON/COR	...	...	...	-487.55±0.09
Adopted	49.58±0.20	42.81±0.2	7414±30	-487.5±0.4

TABLE 2-5. Temperature of fusion of LiOH.

Reference	$T_{\text{fus}}/^\circ\text{C}$	$T_{\text{fus}}/\text{K}$	Comments
Original Studies			
15SCA	462	735	Thermal analysis
51DIO	477	750	Thermal analysis, visual method
52RES/DIO	477	750	Thermal analysis, visual method
53KHI/KHI	462	735	Thermal analysis (DTA)
55SHO/COH	470	744.3	Thermal analysis
58RES/UNZ,	477	743	Thermal analysis (DTA);
59RES/UNZ		750	Thermal analysis, visual method
59ROL/COH	473±0.3	746	Thermal analysis (DTA)
61COH/MIC	473	746	... the LiOH contained
64PER/RES	475	748	0.04% Li <sub>2</sub> CO <sub>3</sub>
67RES/BAR,	477	750	Thermal analysis (DTA)
69RES/BAR			Thermal analysis, visual method
67MIC, 68MIC	474±1	747	Thermal analysis (DTA)
690ST/ITK,	477±1	750	Thermal analysis, visual method;
74POR/ITK	473	746	Thermal analysis (DTA);
	470-475	743-748	Thermal analysis (DTA)
71ADO,	473	746	Thermal analysis (DTA)
71MIC/ERB			
Reviews			
82GUR/VEY		746±2	Based on 9 studies
85CHA/DAV		744.3	Based on 55SHO/COH
Adopted			
This study		746±2	

TABLE 2-6. Enthalpy of fusion of LiOH.

Reference	$\Delta_{\text{fus}}H$	Comments
		$\text{kJ mol}^{-1}$
Original Studies		
54POW/BLA	21.04	Enthalpy measurements
55SHO/COH	20.96	Enthalpy measurements
67RES/BAR	$22.1 \pm 2$	Thermal analysis
71MIC/ERB	20.3	Calculation from data for system LiOH-Ba(OH)
77TYE/DES	24.3	Enthalpy measurements
84TET/JOH	$22.6 \pm 1.7$	Calculation from data for $\Delta_{\text{sub}}H$ and $\Delta_{\text{vap}}H$
Reviews		
82GUR/VEY	$20.9 \pm 1.3$	Based on 55SHO/COH
85CHA/DAV	20.878	Based on 55SHO/COH
Adopted		
This study	$20.9 \pm 0.4$	Based on 55SHO/COH

TABLE 2-7. Thermal functions of LiOH(cr) below 298.15 K.

$T$ K	$C_p^\circ(T)$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ(T) - H^\circ(0)$ $\text{J mol}^{-1}$	$S^\circ(T)$ $\text{J K}^{-1} \text{mol}^{-1}$
15	0.290	1.10	0.096
20	0.684	3.26	0.218
25	1.239	8.00	0.427
30	1.811	15.6	0.702
35	2.558	26.5	1.036
40	3.325	41.2	1.427
45	4.171	59.9	1.868
50	4.934	82.7	2.347
60	6.656	140	3.392
70	8.438	216	4.552
80	10.360	310	5.801
90	12.441	423	7.141
100	14.630	559	8.564
120	19.332	898	11.641
140	23.939	1331	14.970
160	28.319	1854	18.458
180	32.355	2461	22.028
200	36.050	3146	25.633
220	39.433	3901	29.229
240	42.493	4721	32.795
260	45.263	5599	36.306
280	47.776	6530	39.755
298.15	49.580	7414	42.810

TABLE 2-8. Differences (in  $\text{J K}^{-1} \text{mol}^{-1}$ ) between the thermal functions of LiOH(cr and liq) calculated in the present work and in [82GUR/VEY] and in [85CHA/DAV].

$T$ K	[Present work - 82GUR/VEY] $\Delta C_p^\circ(T)$	$\Delta \Phi^\circ(T)$	$\Delta S^\circ(T)$	[Present work - 85CHA/DAV] <sup>a</sup> $\Delta C_p^\circ(T)$	$\Delta \Phi^\circ(T)$	$\Delta S^\circ(T)$
298.15	0	-0.023	0.05	-0.01	-0.005	-0.010
1000	0	-0.041	0.05	0.214	-0.064	-0.005
2000	0	-0.045	0.05	0.214	0.010	0.095

<sup>a</sup>The values of  $\Phi^\circ(T)$  tabulated in [85CHA/DAV] are adjusted to the reference temperature  $T=0$  from 298.15 K.

TABLE 2-9. The enthalpy of formation of LiOH(cr) from measurements of the enthalpy of solution of lithium hydroxide in water.

Authors	Moles of $\text{H}_2\text{O}$ $n$	No. of $T/\text{K}$ meas.	$\Delta_{\text{aq}}H^\circ(T)^a$ $\text{kJ mol}^{-1}$	$\Delta_{\text{aq}}H^\circ$ at 298.15 K $\text{kJ mol}^{-1}$	$\Delta_f H^\circ$ (LiOH, cr, 298.15 K) $\text{kJ mol}^{-1}$	
[1884TRU]	...	...	1	-24.35	-25.0 <sup>d</sup>	-483.5
[06FOR]	111	297.15	1	-18.73	-20.9 <sup>e</sup>	-487.6
(see also [08FOR])						
[33UED]	400	298.15	4	$-20.45 \pm 0.40$	$-21.1 \pm 0.4$	$-487.4 \pm 0.4$
(see also [31UED])						
[61RES]	400	298.15	7	$-22.92 \pm 0.03$	$-23.56 \pm 0.03^f$	$-484.9 \pm 0.3$
[89KON/COR2]	5159	298.15	4	$-20.83 \pm 0.06^g$	$-21.03 \pm 0.06^g$	$-487.5 \pm 0.1$

<sup>a</sup>Reaction is  $\text{LiOH}(\text{cr}) + n\text{H}_2\text{O}(\text{liq}) = \text{LiOH}(\text{soln}, n\text{H}_2\text{O})$ .

<sup>b</sup>Reaction is  $\text{LiOH}(\text{cr}) + \infty\text{H}_2\text{O}(\text{liq}) = \text{Li}^+(\text{soln}, \infty\text{H}_2\text{O}) + \text{OH}(\text{soln}, \infty\text{H}_2\text{O})$ ; recalculated using the enthalpies of dilution of LiOH(soln,  $n\text{H}_2\text{O}$ ) to infinite dilution recommended by Parker [65PAR].

<sup>c</sup>The values were obtained using the value  $\Delta_{\text{aq}}H^\circ(298.15 \text{ K})$  and values recommended by CODATA [89COX/WAG] (in  $\text{kJ mol}^{-1}$ ):  $\Delta_f H^\circ(\text{OH}^-, \text{soln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -230.015 \pm 0.040$ ;  $\Delta_f H^\circ(\text{Li}^+, \text{soln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -278.47 \pm 0.08$ . The uncertainties were calculated as a square root from the sum of squares of the uncertainties of these three values.

<sup>d</sup>Estimated taking conditionally  $n=400$ .

<sup>e</sup>The recalculation of the Forcrand result [06FOR] was carried out by Parker [65PAR] taking into account of the atomic weights changes and the correction for transition to the standard temperature and infinite dilution.

<sup>f</sup>The uncertainties were increased to  $\pm 0.3 \text{ kJ mol}^{-1}$  due to the possible presence of some impurities in the LiOH sample.

<sup>g</sup>The uncertainty given in [89KON/COR2] was recalculated using Student's criterion.

TABLE 2-10. The enthalpy of formation of LiOH(cr) based on dissociation pressure measurements for the reaction:  $2\text{LiOH}(\text{cr}, \text{liq}) = \text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g})$  ( $\text{kJ mol}^{-1}$ ).

Authors	Method	$\Delta_f H^\circ$ (298.15 K)		$\Delta_f H^\circ$ (298.15 K) <sup>b</sup>
		Second law <sup>a</sup>	Third law <sup>a</sup>	Third law
[08JOH]	Static, 793–1176 K, 10 points	$125 \pm 11$	$203.5 \pm 8.1$	$-521.6 \pm 4.2$
[53DIT/JOH]	Effusion, 648–736 K, 11 points;	$158 \pm 35$	$165.1 \pm 1.4$	$-502.4 \pm 0.8$
	Effusion, 752–795 K, 7 points	$169 \pm 107$	$164.6 \pm 1.8$	$-502.1 \pm 1.1$
[55GRE/MOH]	Transpiration and effusion, 523–673 K <sup>c</sup>	$134.5 \pm 2.7$	$136.6 \pm 0.4$	$-488.2 \pm 0.4$
[60BER/MES]	Mass-spectrometric/effusion technique, 490–610 K, 6 points	$146 \pm 36$	$132.4 \pm 2.5$	$-486.0 \pm 1.3$
[84TET/JOH]	Transpiration method, 573–742 K, 25 points;	$136.0 \pm 5.6$	$136.9 \pm 0.3$	$-488.3 \pm 0.4$
	Transpiration, 757–890 K, 8 points	$154 \pm 15$	$136.8 \pm 0.8$	$-488.2 \pm 0.7$
[89MUN/NIS]	Transpiration, 620–744 K, 19 points <sup>c</sup>	$114.6 \pm 0.5$	$136.2 \pm 1.9$	$-487.9 \pm 1.0$
	Transpiration, 744–1020 K, 5 points <sup>d</sup>	$142.4 \pm 1.2$	$137.1 \pm 0.9$	$-488.4 \pm 0.8$
[91TER/MOH]	Transpiration, 569–744 K, 27 points	$130.8 \pm 4.5$	$135.5 \pm 0.4$	$-487.6 \pm 0.4$
	Transpiration, 749–820 K, 10 points	$132.1 \pm 2.8$	$135.8 \pm 0.1$	$-487.7 \pm 0.5$

<sup>a</sup>The uncertainties include only the reproducibility of measurements.

<sup>b</sup>Auxiliary quantities for  $\Delta_f H^\circ(\text{Li}_2\text{O}, \text{cr}, 298.15 \text{ K})$  ( $-597.88 \pm 0.30 \text{ kJ mol}^{-1}$ ) and  $\Delta_f H^\circ(\text{H}_2\text{O}, \text{g}, 298.15 \text{ K})$  ( $-241.814 \pm 0.042 \text{ kJ mol}^{-1}$ ) are taken from 82GUR/VEY. The uncertainty of  $\Delta_f H^\circ(\text{LiOH}, \text{cr}, 298.15 \text{ K})$  is calculated as one half of the value equal to the square root of the sum of squares of the uncertainty of  $\Delta_f H^\circ(298.15 \text{ K})$  (third law), including inaccuracies of the thermal functions of LiOH(cr, liq),  $\text{Li}_2\text{O}(\text{cr})$  and  $\text{H}_2\text{O}(\text{g})$ , and the uncertainties of  $\Delta_f H^\circ(\text{Li}_2\text{O}, \text{cr}, 298.15 \text{ K})$  and  $\Delta_f H^\circ(\text{H}_2\text{O}, \text{g}, 298.15 \text{ K})$  values.

<sup>c</sup>The data were given in the equation form.

TABLE 2-11. Experimental data on the equilibrium constants ( $K/\text{atm}$ ) at different temperatures ( $T/\text{K}$ ) for the reaction:  $2\text{LiOH}(\text{cr}, \text{liq}) = \text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g})$ .

1. [08JOH]		2. [53DIT/JOH]		3. [60BER/MES]	
$T/\text{K}$	$K$	$T/\text{K}$	$K \cdot 10^6$	$T/\text{K}$	$K \cdot 10^4$
793	0.0026316	648	0.55	490	0.15
823	0.0092105	663	2.084	533	0.7
883	0.0302632	677	2.140	545	3.0
943	0.0815789	692	6.645	578	25.0
997	0.1592105	707	6.141	595	60.0
1038	0.2592105	707	5.609	610	80.0
1085	0.4236842	722	14.890		
1119	0.5460526	722	16.340		
1156	0.7289474	736	15.880		
1176	0.8565789	736	12.990		
		736	35.360		
		752	41.650		
		752	36.580		
		766	83.910		
		766	36.390		
		781	65.800		
		781	54.970		
		795	134.0		
4. [84TET/JOH]					
$T/\text{K}$	$-\log K$	$T/\text{K}$	$-\log K$	$T/\text{K}$	$-\log K$
573.1	5.230	639.0	4.110	741.8	2.660
576.0	5.190	660.9	3.620	757.0	2.320
593.1	4.920	662.3	3.620	783.7	2.080
618.8	4.470	663.1	3.620	791.1	2.250
623.1	4.270	663.1	3.620	801.3	2.150
639.0	4.110	664.0	3.620	811.0	2.080
641.0	3.920	664.9	3.620	846.0	1.920
650.2	3.850	679.8	3.400	870.3	1.770
650.2	3.850	682.1	3.420	889.7	1.680
653.2	3.810	683.1	3.380	656.2	3.770
684.9	3.290	657.9	3.860	719.9	2.950
5. [91TER/MOH]					
569.5	5.133	678.8	3.310	749.1	2.413
589.3	4.677	688.8	3.170	754.2	2.398
599.2	4.531	698.8	3.034	759.2	2.358
609.1	4.416	708.9	2.902	769.2	2.278
609.1	4.395	718.9	2.784	779.3	2.220
619.0	4.211	718.9	2.776	779.3	2.207
628.9	4.062	729.0	2.669	789.4	2.145
638.9	3.898	729.0	2.661	799.4	2.081
638.9	3.898	729.0	2.657	809.5	2.017
648.8	3.907	729.0	2.652	819.6	1.958
658.8	3.601	739.0	2.534		
668.7	3.467	744.1	2.462		
668.7	3.449	744.1	2.458		
669.5	3.747				

TABLE 2-12. Thermodynamic properties of 0.1 MPa: LiOH(cr and liq).

T(K)	$C_p^\circ$	$-(G^\circ - H^\circ(0))T^{-1}$	$S^\circ$	$H^\circ - H^\circ(0)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
	J (mol K) <sup>-1</sup>			kJ mol <sup>-1</sup>		
0	0.000	0.000	0.000	0.000	-481.708	-481.708
25	1.239	0.107	0.427	0.008	-482.330	-479.983
50	4.934	0.693	2.347	0.083	-483.090	-477.356
75	9.370	1.698	5.165	0.260	-483.879	-474.315
100	14.630	2.974	8.564	0.559	-484.593	-471.015
150	26.193	6.159	16.699	1.581	-485.768	-463.958
200	36.050	9.903	25.633	3.146	-486.653	-456.519
250	43.892	13.946	34.558	5.153	-487.200	-488.917
300	49.782	18.098	43.117	7.506	-487.508	-441.233
350	54.456	22.253	51.160	10.118	-487.625	-433.509
400	58.065	26.341	58.676	12.934	-487.621	-425.777
450	61.055	30.328	65.693	15.914	-487.559	-418.050
500	63.660	34.197	72.263	19.033	-490.451	-410.026
600	68.197	41.561	84.281	25.632	-489.877	-393.987
700	72.235	48.450	95.102	32.656	-488.890	-378.078
746 cr	73.994	51.471	99.755	36.020	-488.310	-370.814
746 liq	87.300	51.471	127.771	56.920	-467.410	-370.814
800	87.300	56.829	133.872	61.634	-465.970	-363.873
900	87.300	65.972	144.154	70.364	-463.324	-351.271
1000	87.300	74.258	153.352	79.094	-460.710	-338.960
1100	87.300	81.833	161.673	87.824	-458.133	-326.912
1200	87.300	88.807	169.269	96.554	-455.598	-315.094
1300	87.300	95.269	176.257	105.284	-453.109	-303.486
1400	87.300	101.288	182.726	114.014	-450.671	-292.070
1500	87.300	106.920	188.749	122.744	-448.288	-280.824
1600	87.300	112.212	194.383	131.474	-445.966	-269.735
1700	87.300	117.203	196.676	140.204	-588.555	-251.779
1800	87.300	121.925	204.666	148.934	-585.431	-232.060
1900	87.300	126.405	209.386	157.664	-582.341	-212.512
2000	87.300	130.667	213.864	166.394	-579.284	-193.129
298.15	49.579	17.943	42.810	7.414	-487.500	-441.518
Uncertainties						
0	0.000	0.000	0.001	0.000	0.100	0.100
298.15	0.100	0.150	0.200	0.030	0.100	0.100
1000	0.800	0.600	0.800	0.700	0.700	0.700
2000	5.000	3.000	5.000	5.000	5.000	6.000

## 2.2. Lithium Hydroxide in Gaseous Phase

### 2.2.1. Lithium Hydroxide Monomer

#### Molecular Constants of LiOH

[32LEC]

Lechner calculated the vibrational frequencies of the LiOH molecule using the simple force field approximation.

[53SMI/SUG]

Smith and Sugden estimated the molecular constants of LiOH using an ionic model and assuming a linear structure of the molecule.

[60BER/MES]

Berkowitz *et al.* estimated the molecular constants of LiOH assuming a nonlinear structure by analogy with Li<sub>2</sub>O and H<sub>2</sub>O molecules. These authors studied experimentally the reaction of water vapor with lithium oxide.

[63MCB/HEI]

McBride *et al.* estimated the molecular constants of the LiOH molecule assuming a nonlinear structure of the molecule, based on similarity with the H<sub>2</sub>O and Li<sub>2</sub>O molecules.

[66BUE/PEY]

Buenker and Peyerimhoff carried out an *ab initio* calculation of the geometry of the LiOH molecule using a simple basis set.

[70FRE] (see also [70FRE/GOD], [72FRE/HER], [78LOV])

Freund carried out a molecular beam electric resonance study of LiOH and LiOD in the radio-frequency and microwave regions. The publication [70FRE] was not available at the time of this review; the geometries of <sup>7</sup>LiOH and <sup>7</sup>LiOD obtained in [70FRE] are cited in [72FRE/HER].

[77DIL/SCH]

Dill *et al.* performed an *ab initio* calculation of the LiOH molecule geometry employing a single-determinant MO theory. They used the minimal STO-3G basis set which in-



cluded a full set of  $p$  functions on Li together with standard molecular scaling factors. A linear structure of the LiOH molecule was obtained during geometry optimization.

[79YOS/HAS]

Yoshida and Hase measured IR active fundamental frequencies of four isotopic modifications of polycrystalline LiOH ( $^6\text{LiOH}$ ,  $^6\text{LiOD}$ ,  $^7\text{LiOH}$ , and  $^7\text{LiOD}$ ). The four observed fundamentals belonged to one internal stretching (O-H) mode, two translational lattice modes, and one acoustic mode.

[79ZYU/CHA]

Zyubina and Charkin carried out an *ab initio* calculation of the geometry of the LiOH molecule.

[80NEM/STE] (see also [79NEM/STE])

Nemukhin and Stepanov applied the diatomics-in-molecules approach for the theoretical calculation of the ground-state equilibrium geometry and vibrational frequencies of the LiOH molecule.

[81TAM/SZA]

Tamássi-Lentei and Szaniszló carried out a calculation of the geometry of LiOH using the simplified *ab initio* method based on a Slater determinant composed of floating type (off-center) one-electron spherical Gaussians.

[82GUR/VEY]

Gurvich and co-workers calculated the vibrational frequencies of linear LiOH using the simple valence force field approximation assuming  $f_{\text{Li-O}}=2.13 \times 10^5 \text{ dyn cm}^{-1}$  and  $f_{\alpha}/r_1 r_2=0.04 \text{ dyn cm}^{-1}$ , estimated by comparison with related molecules. The moment of inertia of LiOH was derived from the rotational constant reported in [70FRE].

[82HOU/LEV]

Hout *et al.* calculated the *ab initio* harmonic frequencies of LiOH using the 6-31G\* basis set and applying the Møller-Plesset perturbation theory of the second order to take the electron correlation into account.

[82LUT/ECK]

Lutz *et al.* measured O-H stretching frequency of solid LiOH in IR and Raman spectra.

[82RAG]

Raghavachari investigated the  $\text{H}_2\text{O-Li}_2\text{O}$  system by *ab initio* methods with the 3-21G and 6-31G\* basis sets. Electron correlation was included by using Møller-Plesset perturbation theory up to the third order. The harmonic frequencies of the LiOH molecule were calculated using the 3-21G basis set; for the calculation of the geometry, the larger 6-31G\* set was used.

[83SOL/POG] (see also [83SOL], [83SOL/POG2], [90POG])

Solomonik and co-workers performed *ab initio* calculations for the LiOH molecule using the MO LCAO SCF method. The geometry and harmonic frequencies of the molecule were obtained with basis sets of various sizes. The largest set used for LiOH was Li 9s4p/4s2p, O 10s6p/5s3p,

and H 5s2p/3s1p. For O, the set was augmented by polarization d-functions.

[84RAM/ABA] (see also [79ABA/DEM], [80ABA/DEM])

Rambidi and co-workers carried out *ab initio* calculations of the geometry and harmonic frequencies for LiOH. The following Gaussian atomic basis set was used: Li 9s2p/4s2p, O 9s5p/4s2p, and H 6s1p/2s1p. Additionally, a d-function contribution was used for the O atom.

[85CHA/DAV]

Chase and co-workers calculated the moment of inertia for linear LiOH molecule using the rotational constant  $B_{0,0,0}$  reported in [70FRE]; the vibrational frequencies were estimated in the simple valence force field approximation using the following values of the force constants:  $F_{11}=1.15 \text{ m dyn } \text{Å}^{-1}$ ,  $F_{22}=0.060 \text{ m dyn } \text{Å}^{-1}$ , and  $F_{33}=7.5 \text{ m dyn } \text{Å}^{-1}$ . These values were obtained by extrapolation of the data [69ACQ/ABR] on the other alkali hydroxides.

[85MAN/LOU]

Manceron *et al.* studied the reaction of Li with  $\text{H}_2\text{O}$  using Kr matrix isolation IR spectroscopy.  $^6\text{Li}/^7\text{Li}$  and H/D isotopic substitutions and irradiation effects in both visible and near IR regions permitted the identification of the formation of the LiOH molecule by two absorptions below  $1000 \text{ cm}^{-1}$  attributed to the Li-O stretching and the Li-O-H bending modes of this molecule. This assignment was confirmed by normal coordinate calculations assuming a linear structure of the molecule. The unobserved O-H stretching frequency was calculated from the force field.

[85NEM/LYU]

Nemukhin *et al.* carried out an *ab initio* calculation of the energies of the isomers HLiO and LiHO relative to the more stable LiOH molecule and of the energies of the excited electronic states of the LiOH molecule. For the LiHO isomer not investigated, it was found  $r(\text{Li-H})=2.75 \text{ a.u.}$  and  $r(\text{H-O})=1.92 \text{ a.u.}$

[86BAU/LAN]

Bauschlicher *et al.* carried out *ab initio* calculations of the values of  $r(\text{Li-O})$ ,  $\nu(\text{Li-O})$ , and  $D_0(\text{Li-OH})$  of LiOH in the ground electronic state using both the self-consistent field (SCF) and singles plus doubles configuration (CISD) levels and an extended Gaussian basis set of at least triple-zeta plus double polarization quality.

[86DYK/FEH]

Dyke *et al.* performed *ab initio* molecular orbital calculations for the LiOH molecule. The following Gaussian atomic basis set was used: Li 5s2p, O 4s2p, and H 3s. This set was augmented by one polarization function on each center. Molecular geometry was optimized utilizing analytical gradient techniques as implemented in the GAMESS program. The force constant matrix was constructed and diagonalization of this matrix yielded vibrational frequencies for the normal modes.

[87MCN/TAC]

McNaughton *et al.* measured the microwave transitions of  $^7\text{Li}^{16}\text{OH}$  and  $^7\text{Li}^{16}\text{OD}$  up to  $J=5$  in both ground and excited

bending vibrational states and those of  ${}^7\text{Li}^{18}\text{OH}$  in the ground state only. The form of the bending potential was analyzed. The LiOH molecule was found to be linear in its equilibrium configuration.

[89BUN/JEN] (see also [77LIS/CAR])

Bunker and co-workers calculated the three-dimensional potential energy surface of the LiOH molecule at 166 nuclear geometries covering ranges of about  $2500\text{ cm}^{-1}$  for Li-O stretch,  $7500\text{ cm}^{-1}$  for the O-H stretch, and  $4000\text{ cm}^{-1}$  for the Li-O-H bond. They used an *ab initio* configuration interaction approach within the framework of average coupled pair functional method and a Morse oscillator-rigid bender internal dynamics Hamiltonian for variational calculation. The following Gaussian basis set was used: Li9s4p1d/4s2p1d, O12s8p4d1f/6s5p3d1f, and H6s2p/3s2p. This set was augmented by further polarization functions for all three atoms. The calculations were performed with the COLUMBUS program system. The rotational-vibrational energy levels of  ${}^7\text{Li}^{16}\text{OH}$ ,  ${}^7\text{Li}^{16}\text{OD}$ , and  ${}^7\text{Li}^{18}\text{OH}$  were calculated.

[90BEL/LEB]

Belyayev *et al.* estimated the bending frequency  $\nu_2$  of the LiOH molecule from the analysis of the results of the spectrophotometric studies of chemical equilibria in flames. The estimated value provided the best consistency between their second and third law treatments of experimental data.

#### Discussion of the Molecular Constants of LiOH(g)

Investigations of the gaseous LiOH molecule, both theoretical [66BUE/PEY, 77DIL/SCH, 77LIS/CAR, 79ZYU/CHA, 81TAM/SZA, 82HOU/LEV, 82RAG, 83SOL/POG, 84RAM/ABA, 86BAU/LAN, 86DYK/FEH, 89BUN/JEN] and experimental [70FRE, 85MAN/LOU, 87MCN/TAC], provide strong evidence in support of a linear configuration in the ground electronic state  $X^1\Sigma^+$ . In earlier equilibrium studies (see [60BER/MES, 66JEN/PAD, 69COT/JEN]) the bent configuration of LiOH was assumed on the basis of similarity to the  $\text{H}_2\text{O}$  and  $\text{Li}_2\text{O}$  molecules following the estimates made in the old editions of JANAF Thermochemical Tables (before 1971). On the other hand, the linear structure of the LiOH molecule was predicted on the basis of the ionic model as long ago as in 1953 by Smith and Sugden [53SMI/SUG] who investigated stability of gaseous lithium hydroxide in flames.

The investigation of the rotational spectra of LiOH and LiOD by Freund [70FRE] unambiguously proved the linearity of this molecule, and numerous subsequent *ab initio* calculations successfully confirmed this conclusion. The values of the Li-O bond length calculated by different authors (see Table 2-13) are in excellent agreement with each other except for some low level calculations (such as [79ZYU/CHA, 81TAM/SZA]) and the estimates based on the analogy with the  $\text{Li}_2\text{O}$  molecule [53SMI/SUG, 60BER/MES, 63MCB/HIE].

The LiOH molecule has three fundamental frequencies:  $\nu_1$  (Li-O stretching),  $\nu_2$  (doubly degenerate Li-O-H bending), and  $\nu_3$  (O-H stretching). The spectral determinations of  $\nu_1$  were reported by Freund [70FRE] and Smith [72SMI],

but the details of the experiments are not available. Spectral data on LiOH obtained by Linevsky [68LIN] are also unavailable to us. The most reliable experimental data on the fundamental frequencies of LiOH were obtained by Manceron *et al.* [85MAN/LOU] who identified the IR absorption spectrum of the lithium hydroxide molecules isolated in a Kr matrix and assigned  $\nu_1$  for  ${}^7\text{LiOH}$ ,  ${}^6\text{LiOH}$ ,  ${}^7\text{LiOD}$ ,  ${}^6\text{LiOD}$  and  $\nu_2$  for  ${}^7\text{LiOH}$  and  ${}^6\text{LiOH}$ . The value of  $\nu_3$  was calculated in [85MAN/LOU] from the normal coordinate analysis. The values of vibrational frequencies of the LiOH molecule obtained from theoretical calculations (these calculations mostly yield harmonic frequencies) are presented in Table 2-13. As a rule, these values differ appreciably from each other; besides, all calculated values of  $\nu_2$  are larger than the experimental values. The best approach to the latter was the comprehensive *ab initio* calculation by Bunker *et al.* [89BUN/JEN].

In the *ab initio* study [85NEM/LYU] (see also [79CHA/ZYU2]) it was shown that the HLiO and LiHO isomers are about 300 and 600  $\text{kJ mol}^{-1}$ , respectively, less stable than LiOH.

The values of the molecular constants of LiOH reported in the literature are presented in Table 2-13. A number of old spectral studies of LiOH in crystalline state, films or solutions are not included in the table.

Selection of the structural parameters of LiOH for calculation of the thermal functions is rather ambiguous because of the unavailability of information about details of the only two experimental studies of the rotational spectra of this molecule. These studies are known only in abstract publications [70FRE, 87MCN/TAC]. In the review on microwave spectra of triatomic molecules Lovas [87LOV] gives the values of the rotational constants  $B_{0,0,0}=35342.44(5)$  and  $31477.39(5)$  MHz for  ${}^7\text{Li}^{16}\text{OH}$  and  ${}^7\text{Li}^{16}\text{OD}$ , respectively, and  $r_e(\text{Li-O})=1.580$  and  $r_e(\text{O-H})=0.950$  Å for this molecule with the reference to a personal communication by Freund in 1986. The same values are given in [70FRE]. These values of bond lengths are accepted in the present work assuming the uncertainty  $0.005$  Å in both values. The corresponding value of the moment of inertia for natural isotopic composition is  $(2.334 \pm 0.010) \times 10^{-39}$  g  $\text{cm}^2$ . The bond lengths obtained in the best *ab initio* calculations ([89BUN/JEN]) practically coincide with the accepted values.

Selection of the fundamental frequencies of LiOH is also based on the results of experimental work, namely [85MAN/LOU], where the IR spectrum of LiOH was observed in a Kr matrix. The accepted value of  $\nu_1=870.5\text{ cm}^{-1}$  actually agrees with the results of the other works if one assumes the uncertainty of this frequency equal to about  $30\text{ cm}^{-1}$  (possible matrix shift). In the case of  $\nu_2$ , the accepted value is noticeably lower than those obtained from *ab initio* calculations. Only the value obtained in the best theoretical study [89BUN/JEN],  $289\text{ cm}^{-1}$ , is in good agreement with our accepted value,  $256.5\text{ cm}^{-1}$ . We estimate the uncertainty of  $\nu_2$  as  $30\text{ cm}^{-1}$  (similar to  $\nu_1$ ). The  $\nu_3$  frequency is characteristic for many molecules and lies in the vicinity of  $3700\text{ cm}^{-1}$ . The accepted value of  $\nu_3=3687.6\text{ cm}^{-1}$  was out of

the investigated spectral range, but was calculated [85MAN/LOU] in the valence force field approximation. We accept this value because it is consistent with the other two frequencies. The uncertainty in  $\nu_3$  is estimated as  $50 \text{ cm}^{-1}$ .

For LiOH, the symmetry number  $\sigma=1$  and the statistical weight of the ground electronic state  $p_X=1$ .

The existence of low lying excited electronic states of LiOH is not expected. According to [85NEM/LYU], the energy of the lowest excited electronic state of LiOH ( $^3\Pi$ ) is more than 3 eV, and it can be ignored in these calculations.

The molecular constants of LiOH, adopted in the present work for calculation of the thermal functions, are summarized as follows:

$$\begin{aligned} r(\text{Li-O}) &= 1.580 \pm 0.005 \text{ \AA}; \\ r(\text{O-H}) &= 0.950 \pm 0.005 \text{ \AA}; \\ \langle \text{Li-O-H} \rangle &= 180^\circ; \\ I &= (2.334 \pm 0.010) 10^{-39} \text{ g cm}^2; \\ \sigma &= 1; \quad p_X = 1; \\ \nu_1 &= 870.5 \pm 30 \text{ cm}^{-1}, \quad d_1 = 1; \\ \nu_2 &= 256.5 \pm 30 \text{ cm}^{-1}, \quad d_2 = 2; \\ \nu_3 &= 3687.6 \pm 50 \text{ cm}^{-1}, \quad d_3 = 1. \end{aligned}$$

TABLE 2-13. Bond lengths (Å), angle (deg), and vibrational frequencies ( $\text{cm}^{-1}$ ) of LiOH in the ground electronic state.

Reference	$r(\text{Li-O})$	$r(\text{O-H})$	$\langle \text{Li-O-H} \rangle$	$\nu_1$	$\nu_2$	$\nu_3$	Note
[32LEC]	...	...	...	980	1260	3700	a
[35SMI/SUG]	1.82	0.97	180	800	410	3840	a
[60BER/MES]	1.82	0.96	107	665	1250	3700	b
[63MCB/HEI]	1.82	0.95	105	1070	1120	3710	c
[70FRE]	1.580	0.950	180	739	...	...	d
(cit. in [72FRE/HER])							
[72SM]	...	...	...	746	...	...	e
[77DIL/SCH]	1.432	0.971	180	...	...	...	f
[79YOS/HAS]	...	...	...	...	...	3679	g
[79ZYU/CHA]	1.540	0.953	180	...	...	...	f
[80NEM/STE]	1.582	0.958	180	861	313	3868	h
[81TAM/SZA]	1.46	0.88	180	...	...	...	f
[82GUR/VEY]	1.595	0.926	180	850	370	3700	i
[82HOU/LEV]	...	...	180	1000	295	3964	f
[82LUT/ECK]	...	...	...	...	...	3570	g
[82RAG]	1.592	0.938	180	1162	467	4011	f
[83SOL]	1.606	0.937	180	936	334	4318	f
[84RAM/ABA]	1.571	0.943	180	980	475	4264	f
[85CHA/DAV]	1.582	0.971	180	630	362	3666	i
[85MAN/LOU]	...	...	180	870.5	256.5	3687.6	e
[86BAU/LAN]	1.573	...	180	931	...	...	f
[86DYK/FEH]	1.596	0.933	180	984	431	4295	f
[89BUN/JEN]	1.5857	0.9499	180	923	289	3832	f
[90BEL/LEB]	...	...	180	...	300	...	a
Accepted in the present work	1.580	0.950	180	870.5	256.5	3687.6	j

<sup>a</sup>Estimated.

<sup>b</sup>Estimated for bent structure;  $\nu_2$  is singly degenerate.

<sup>c</sup>Estimated for bent structure;  $\nu_2$  is singly degenerate.

<sup>d</sup>Microwave spectrum.

<sup>e</sup>Matrix-isolated IR spectrum.

<sup>f</sup>*Ab initio* calculation.

<sup>g</sup>IR spectrum of crystal.

<sup>h</sup>Diatomics-in-molecules theoretical calculation.

<sup>i</sup>Geometry is based on the data from [70FRE]; frequencies are calculated in the simple valence force field approximation.

<sup>j</sup>Geometry from [70FRE], frequencies from [85MAN/LOU].

TABLE 2-14. Differences (in  $\text{J K}^{-1} \text{mol}^{-1}$ ) between the thermal functions of  $\text{LiOH}(\text{g})$  calculated in the present work and in [82GUR/VEY, 85CHA/DAV].

T, K	Present work-[82GUR/VEY] <sup>a</sup>			Present work-[85CHA/DAV] <sup>b</sup>		
	$\Delta C_p^\circ(T)$	$\Delta \Phi^\circ(T)$	$\Delta S^\circ(T)$	$\Delta C_p^\circ(T)$	$\Delta \Phi^\circ(T)$	$\Delta S^\circ(T)$
298.15	1.697	2.528	4.911	-0.104	2.163	3.715
1000	0.171	4.635	5.719	-0.300	3.000	3.133
2000	0.056	5.199	5.789	-0.108	3.025	3.001
3000	0.028	5.400	5.806	-0.555	3.010	2.970
4000	0.017	5.502	5.812	-0.032	2.998	2.900
5000	0.012	5.567	5.817	-0.020	2.993	2.954
6000	0.008	5.609	5.819	-0.014	2.985	2.951

<sup>a</sup>The values of  $\Phi^\circ(T)$  and  $S^\circ(T)$  tabulated in [82GUR/VEY] are recalculated to the standard pressure 0.1 MPa.

<sup>b</sup>The values of  $\Phi^\circ(T)$  tabulated in [85CHA/DAV] are adjusted to the reference temperature  $T=0$  from 298.15 K.

#### Calculation of the $\text{LiOH}(\text{g})$ Thermal Functions

The thermal functions of  $\text{LiOH}(\text{g})$  in the standard state are calculated in the "rigid rotor-harmonic oscillator" approximation with low-temperature quantum corrections according to the equations given in [89GUR/VEY]. The calculated values of  $C_p^\circ(T)$ ,  $\Phi^\circ(T)$ ,  $S^\circ(T)$ ,  $H^\circ(T)$ ,  $H^\circ(0)$  in the temperature range 0–6000 K are given in Table 2-20.

The uncertainties in the thermal functions of  $\text{LiOH}(\text{g})$  are mainly due to the uncertainties of the fundamental frequencies as determined in the matrix isolation studies. The largest contribution to the uncertainties arises from the uncertainty of the accepted value of the bending frequency,  $\nu_2$ . At high temperatures, an additional contribution to the uncertainty is the approximate method of calculation. In particular, the neglect of the centrifugal distortion of the  $\text{LiOH}$  molecule may result in the errors from 0.001 to 0.15  $\text{J K}^{-1} \text{mol}^{-1}$  for  $\Phi^\circ(T)$  in the range  $T=298.15$ –4000 K and about twice as much for  $S^\circ(T)$ . The total uncertainties in the thermal functions of  $\text{LiOH}(\text{g})$  are presented in Table 2-20.

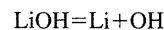
The thermal functions of  $\text{LiOH}(\text{g})$  were calculated earlier in [60BER/MES] (500–1100 K), [62WIL/LOD] (298.15–5000 K), the molecular constants estimated in [53SMI/SUG] were used, [63MCB/HEI] (298.15–6000 K), [82GUR/VEY] (100–6000 K), [83SOL] (298.15–3000 K), and [85CHA/DAV] (100–6000 K). The use of some new data in the present work results in differences of the thermal functions from those recommended in [82GUR/VEY] and [85CHA/DAV]; the comparison of the thermal functions for  $\text{LiOH}(\text{g})$  at numerous temperatures is shown in Table 2-14.

#### Enthalpy of Formation of $\text{LiOH}(\text{g})$ —Experimental Investigations of Equilibria in Flames

[53SMI/SUG], [54JAM/SUG], see also [52SMI/SUG], [53JAM/SUG], [55JAM/SUG], [55SUG/WHE]

Smith and Sugden [53SMI/SUG] provided the first information about the stability of lithium hydroxide in flames. They measured the ionization in hydrogen-air flames with lithium compounds added. The ionization was lower than expected from the Saha equation for ionization of free Li atoms. From these measurements, the presence of lithium in two forms was assumed: free lithium atoms and  $\text{LiOH}$  molecules. For  $T=2200$  K, Smith and Sugden calculated the

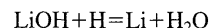
value of the equilibrium constant  $K^\circ(2200)=8 \times 10^{-5}$  (partial pressures in atm) for the gaseous reaction



and from the third-law calculation with a linear model of  $\text{LiOH}(\text{g})$  found the value  $D_0(\text{Li-OH})=102 \pm 1 \text{ kcal mol}^{-1}$  ( $427 \pm 4 \text{ kJ mol}^{-1}$ ). The free hydroxyl partial pressure was calculated assuming attainment of thermal equilibrium in flame gases at a distance of several centimeters above the burner. James and Sugden [54JAM/SUG] confirmed the results of Smith and Sugden using the resonance radiation measurements for the determination of partial pressures of alkali atoms in flames.

[60PHI], [65MCE/PHI], [67MCE/PHI]

McEwan and Phillips [65MCE/PHI] presented equilibrium constant values for the gaseous reaction



at four temperatures:  $T=1400, 1800, 2200$  and  $2600$  K (130, 26.2, 8.95, 4.55, respectively). These values were obtained in Phillips' dissertation [60PHI] using the method of atomic absorption to determine the partial pressure of Li atoms in flames. McEwan and Phillips [65MCE/PHI] mentioned that the values of the equilibrium constant "are based on measurements in high-temperature flames." Later, in [67MCE/PHI], they indicated that in Phillips dissertation [60PHI] the flame photometric measurements were made in the temperature range 2400–2600 K. In our work only the value 4.55 for the highest temperature  $T=2600$  K is used. More convenient for comparison with other flame photometric measurements is the use of the equilibrium constant value  $K^\circ(2600)=0.220$  for the reverse reaction



[66JEN/PAD], [70JEN]

Jensen and Padley studied the formation of  $\text{LiOH}$  molecules in  $\text{H}_2+\text{O}_2+\text{N}_2$  flames with an initial composition  $\text{H}_2:\text{O}_2:\text{N}_2=3.4:1:2$ ; its temperature was determined from D-line reversal measurements, to be  $2475 \pm 15$  K. Steady values of temperature and of metal atom, hydrogen, and electron concentration as a function of distance from the burner

in the region of experimental measurements were assumed to indicate the attainment of thermodynamic equilibrium. The method gave an equilibrium constant value for the reaction  $[\text{Li} + \text{H}_2\text{O} = \text{LiOH} + \text{H}]$ ,  $K^\circ(2475 \text{ K}) = 0.23$ . Third-law calculation, assuming a bent molecule, resulted in the value  $D_0(\text{Li-OH}) = 101 \pm 2 \text{ kcal mol}^{-1}$  ( $423 \pm 8 \text{ kJ mol}^{-1}$ ). Later Jensen [70JEN] reinterpreted the results of Jensen and Padley [66JEN/PAD], using a linear model. He accepted the value  $D_0(\text{LiOH}) = 430 \pm 12 \text{ kJ mol}^{-1}$  as a compromise between calculations for linear and bent models.

#### [69COT/JEN]

Cotton and Jenkins determined the dissociation energy,  $D_0^\circ(\text{Li-OH})$ , using the measurements of the concentration of lithium atoms as a function of hydrogen atom concentration in hydrogen-rich, hydrogen-oxygen-nitrogen flames. A set of 5 isothermal flames ( $T = 2370 \text{ K}$ ) of different composition was used for measurements. Equilibrium constant values for reaction (1) were evaluated from the slope-to-intercept ratio of a linear fit of relative metal atom vs hydrogen-atom concentration. The agreement between the five flames in the set was good. Since the intercept was small and may be subject to systematic errors, the authors [69COT/JEN] calculated a value of the intercept from the atomizer calibration and  $k$ , the absorption coefficient at the center of resonance line. The authors [69COT/JEN] considered the theoretical value to be more accurate; the maximum error was estimated to be 30%. Third-law calculations were made with the data from the JANAF tables (see [71STU/PRO]) using a bent structure for  $\text{LiOH}(\text{g})$ . The following values of dissociation energy were obtained: (i) with the use of experimental values of the intercept,  $D_0(\text{Li-OH}) = 104.1 \pm 0.3 \text{ kcal mol}^{-1}$  ( $435.6 \pm 1.3 \text{ kJ mol}^{-1}$ ); (ii) with the use of theoretical value of the intercept,  $D_0(\text{Li-OH}) = 105.0 \pm 1.0 \text{ kcal mol}^{-1}$  ( $439.3 \pm 4.2 \text{ kJ mol}^{-1}$ ). As the best value with the total error limit Cotton and Jenkins accepted  $D_0(\text{Li-OH}) = 105 \pm 2 \text{ kcal mol}^{-1}$  ( $439 \pm 8 \text{ kJ mol}^{-1}$ ).

Later Zeegers and Alkemade [70ZEE/ALK] concluded that the value of parameter of broadening for lithium resonance line,  $a = 0.5$ , is more appropriate than the value  $a = 0.3$ , as used by Cotton and Jenkins. This higher value of  $a$ -parameter yielded the value of  $k$  and the value  $K^\circ$ , which are lower by a factor of 1.2. In turn, this resulted in a value  $D_0(\text{Li-OH}) = 435.7 \text{ kJ mol}^{-1}$ .

The recalculated data are listed in Table 2-15 and are included in Fig. 2-4.

#### [70ZEE/ALK], [65ZEE]

Zeegers and Alkemade recalculated all data on the dissociation energy of  $\text{LiOH}$  molecule from the literature with the use of thermal functions published by JANAF in 1966 (the assumed molecular structure). They also presented  $D_0$  ( $\text{Li-OH}$ ) values based on the data from Zeegers thesis [65ZEE]: second law,  $D_0(\text{Li-OH}) = 105.3 \pm 2 \text{ kcal mol}^{-1}$  ( $440.6 \pm 8 \text{ kJ mol}^{-1}$ ); third law,  $D_0(\text{Li-OH}) = 107 \pm 2 \text{ kcal mol}^{-1}$  ( $448 \pm 8 \text{ kJ mol}^{-1}$ ). On the basis of the experimental data available, Zeegers and Alkemade recommended

the value  $D_0(\text{Li-OH}) = 104.5 \pm 1 \text{ kcal mol}^{-1}$  ( $437.2 \pm 4 \text{ kJ mol}^{-1}$ ).

#### [71KEL/PAD]

Kelly and Padley made flame photometric studies of Li emission in  $\text{H}_2 + \text{O}_2 + \text{CO}_2$  and  $\text{H}_2 + \text{O}_2 + \text{N}_2$  flames in the temperature range 1950–2750 K. Thirty-three values of the equilibrium constant for reaction (1) were obtained. The data in [71KEL/PAD] were presented only in a graph. Kelly and Padley fitted the equilibrium constant values in the temperature range 1950–2750 K with the equation

$$K^\circ(T) = A \exp(-\Delta_r H^\circ(2350 \text{ K})/RT),$$

where  $\log A = 1.18$ ,  $\Delta_r H^\circ(2350 \text{ K}) = 85 \text{ kJ mol}^{-1}$ .

From the enthalpy of reaction  $[\text{Li} + \text{H}_2\text{O} = \text{LiOH} + \text{H}]$  at the mean temperature of the measurements,  $T = 2350 \text{ K}$ , Kelly and Padley calculated the second and third law values of dissociation energy of  $\text{LiOH}$  for linear and bent models of the molecule:  $D_0(\text{Li-OH}) = 433 \pm 8 \text{ kJ mol}^{-1}$  (second law, linear);  $D_0(\text{Li-OH}) = 430 \text{ kJ mol}^{-1}$  (third law, linear);  $D_0(\text{Li-OH}) = 427 \text{ kJ mol}^{-1}$  (second law, bent);  $D_0(\text{Li-OH}) = 416 \text{ kJ mol}^{-1}$  (third law, bent). They recommended as the best the value  $D_0(\text{Li-OH}) = 433 \text{ kJ mol}^{-1}$ , based on the second law treatment for the linear model. The equation given permits calculation of the following values of  $K^\circ$  for reaction (1) at the lowest, mean and highest temperature of the range: 1950 K,  $K^\circ = 0.080$ ; 2350 K,  $K^\circ = 0.195$ ; 2750 K,  $K^\circ = 0.367$ . These values are included in Fig. 2-4.

#### [90BEL/LEB]

Belyaev, Lebedeva and Krasnov performed extensive flame photometric studies of the equilibrium of the reaction  $[\text{Li} + \text{H}_2\text{O} = \text{LiOH} + \text{H}]$ . They used atomic emission method and made 5 sets of experiments with 25 flames (natural gas + air + oxygen) in the temperature range 2143–2880 K (85 points). Partial pressure values for  $\text{LiOH}$  were calculated from the equation:

$$P(\text{LiOH}) = P\left(\sum \text{Li}\right) - P(\text{Li}) - P(\text{Li}^+) - P(\text{LiO}).$$

In this equation,  $P(\sum \text{Li})$  is the total pressure of lithium atoms and all lithium compounds in a flame.  $P(\sum \text{Li})$  values were calculated from a lithium salt amount introduced in a flame using a calibrated pneumatic atomizer. Calculations performed have shown that partial pressure of  $\text{Li}^+$  ions is less than 10% of total lithium amount in all flames with the temperature  $T < 2800 \text{ K}$ , and that the amount of  $\text{LiO}$  molecules did not exceed 3–4% even in oxidizing flames. The amount of  $\text{LiO}_2$  was estimated to be substantially less than that of  $\text{LiO}$ .

The authors [90BEL/LEB] performed second and third law treatment of all flame photometric measurements (from their work and from [65MCE/PHI], [66JEN/PAD], [69COT/JEN], [71KEL/PAD]) and obtained following values of enthalpy of reaction:

$$\text{second law, } \Delta_r H^\circ(2500 \text{ K}) = 89 \pm 5 \text{ kJ mol}^{-1},$$

$$\Delta_r H^\circ(0) = 66 \pm 5 \text{ kJ mol}^{-1},$$

third law,  $\Delta_r H^\circ(0 \text{ K}) = 58 \pm 1 \text{ kJ mol}^{-1}$ .

The authors [90BEL/LEB] used auxiliary thermodynamic data from [82GUR/VEY]. They recommended the value,  $D_0(\text{Li-OH}) = 428 \pm 5 \text{ kJ mol}^{-1}$ , based on the second law treatment. The equilibrium constant values from this paper [90BEL/LEB] are listed in Table 2-15 and are presented in Fig. 2-4.

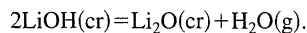
#### Enthalpy of Formation of LiOH(g)—Experimental Investigations of Solid-Gas Equilibria

[55VAN/SPI]

Van Arkel, Spitsbergen and Hyding performed a series of experiments on the dependence of the volatility of lithium oxide in the presence of water vapor. Quantitative data, which could be used for the determination of equilibrium constants of reactions between lithium oxide and water vapor with the formation of gaseous lithium hydroxide molecules, were not obtained.

[59SCH/POR]

Schoonmaker and Porter made an attempt to obtain the mass spectrum of lithium hydroxide vapors. The usual procedure was unsuccessful because "furnace filaments were attacked and destroyed during outgassing" and "the background pressure in the vacuum system was too high to permit operation of the mass spectrometer." The difficulty associated with studying lithium hydroxide was attributed to the process of decomposition:



[60SCH/POR]

Schoonmaker and Porter carried out a mass spectrometric study of high temperature reactions of  $\text{H}_2\text{O}(\text{g})$  and  $\text{HCl}(\text{g})$  with sodium and lithium oxides. In the case of the  $\text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g})$  system,  $\text{Li}^+$  and  $\text{LiOH}^+$  ion species were detected in the temperature range 780–900 °C, with the ratio  $\text{Li}^+/\text{LiOH}^+ \approx 0.1$ . This result may be regarded as the first unambiguous identification of LiOH molecules in vapors over lithium oxide in equilibrium with water vapors. No quantitative data on the partial pressure of LiOH molecules was obtained, however.  $\text{LiOH}^+$  ions were detected also in the system  $\text{Li}_2\text{O}(\text{cr}) - \text{Na}_2\text{O}(\text{cr}) - \text{H}_2\text{O}(\text{g})$  at  $T = 1082 \text{ K}$ .

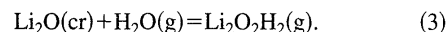
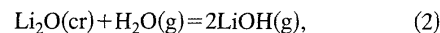
[60BER/MES]

Berkowitz, Meschi and Chupka carried out an extensive mass spectrometric study of interaction of  $\text{Li}_2\text{O}(\text{cr})$  with water vapors. Two types of experiments were performed:

1. Lithium hydroxide or deuterioxide was placed in a Knudsen cell and the assembly heated by radiation. The vapor effusing from the Knudsen cell was bombarded by an electron beam, and the ions produced were mass analyzed with a magnetic mass spectrometer. In this type of experiment the partial pressures of the dimer molecule,  $\text{Li}_2\text{O}_2\text{H}_2$  or  $\text{Li}_2\text{O}_2\text{D}_2$  were obtained.

2. A platinum cell was designed for introduction of vapor from an external source directly into the cell. Water vapor from a reservoir was introduced into the system through a

needle valve, which regulated the flow rate. The pressure of the water vapor on the mass spectrometer side of the needle valve was measured by means of a small McLeod gauge. The cell described made it possible to study the equilibria



The data obtained for the reaction (3) are discussed separately. In this type of experiment, interaction of  ${}^6\text{Li}_2\text{O}(\text{cr})$  ( ${}^6\text{Li}/{}^7\text{Li} \approx 12.5$ ) with  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  ( $\text{D}/\text{H} \approx 5$ ) was studied. The  $\text{H}_2\text{O}$  pressure was monitored at mass 20, corresponding to the  $\text{H}_2^{18}\text{O}^+$  ion, because the mass peak 18 was too intense for the electron multiplier detector system. The measurements were made in the temperature range 1119–1448 K (18 points). The energy of ionizing electrons was 75 eV. A typical mass spectrum, obtained at the temperature  $T = 1350 \text{ K}$  and  $P(\text{H}_2\text{O}) = 0.16 \text{ mm Hg}$ , is given below:

Mass number	Ion	Ion intensity (arbitrary units)
20	$\text{H}_2^{18}\text{O}^+$	$1.76 \times 10^5$
6	${}^6\text{Li}^+$	$2.47 \times 10^6$
23	${}^6\text{LiOH}^+$	$9.18 \times 10^7$
29	${}^6\text{Li}_2\text{OH}^+$	$2.42 \times 10^6$
52	${}^6\text{Li}_3\text{O}_2\text{H}_2^+$	$6.6 \times 10^4$

From the mass spectrum, it followed that the LiOH molecule was the major reaction product; the amount of dimer molecules ( $\text{Li}_2\text{O}_2\text{H}_2$ ), which fragment under electron impact to form  $\text{Li}_2\text{OH}^+$  ions, was much smaller (at the water vapor pressure used), and only traces of trimer molecules ( $\text{Li}_3\text{O}_3\text{H}_3$ ) were detected.

Berkowitz *et al.* calculated equilibrium constant values for reaction (2). No significant differences in equilibrium constant values for reaction (2) were found in experiments with different  $\text{H}_2\text{O}(\text{g})$  and  $\text{D}_2\text{O}(\text{g})$  pressures. The authors [60BER/MES] assumed that the difference of reaction energy for hydrogen- and deuterium-bearing molecules was within the experimental error. The authors summarized the following data for the reaction (2):

$$\text{second law, } \Delta_r H^\circ(1300 \text{ K}) = 78 \pm 3 \text{ kcal mol}^{-1} \\ (326 \pm 13 \text{ kJ mol}^{-1}),$$

$$\text{third law, } \Delta_r H^\circ(1300 \text{ K}) = 80 \pm 2 \text{ kcal mol}^{-1} \\ (335 \pm 8 \text{ kJ mol}^{-1}),$$

based on Gibbs energy functions calculated using a bent model for LiOH(g). The equilibrium constants are listed in Table 2-16 and are presented in Fig. 2-5.

[84TET/JOH2]

Tetenbaum and Johnson performed a transpiration investigation of lithium oxide volatility in helium carrier gas with small amount of water vapors. The total pressure of carrier gas was approximately one atmosphere. The water vapor content in the measurements was in the range between 4 ppm to 555 ppm. The measurements (20 points) were made at temperatures 1023–1273 K.

Comparison with the data of Berkowitz *et al.* [60BER/MES] led the authors [84TET/JOH2] to the conclusion that under the conditions of their experiments, the main process of lithium oxide evaporation was the reaction (2). Least-squares analysis resulted in the following relationship:

$$\log K = -(17269 \pm 659)T^{-1} + (9.13 \pm 0.56).$$

The following second and third law values for the mean temperature were given:

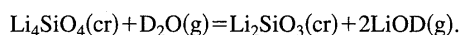
$$\text{second law, } \Delta_f H^\circ(T) = 79.0 \pm 3.0 \text{ kcal mol}^{-1} \\ (330.5 \pm 13 \text{ kJ mol}^{-1});$$

$$\text{third law, } \Delta_f H^\circ(T) = 82.1 \pm 1.0 \text{ kcal mol}^{-1} \\ (343.5 \pm 4.2 \text{ kJ mol}^{-1}).$$

The third-law calculation was performed using entropy values of reaction constituents taken from [60BER/MES]. Equilibrium constant values are listed in Table 2-16 and are presented in Fig. 2-5.

[92PEN/IHL]

Penzhorn, Ihle, Huber, Schuster, and Ache performed a mass spectrometric study of the equilibrium



The sensitivity of the apparatus was calibrated using the intensity of the  $^{107}\text{Ag}^+$  ion at the triple point of silver, 1234 K, where the pressure of silver was taken equal to 0.378 Pa. The ionization cross section of  $\text{D}_2\text{O}$  was taken from [66SCH/DEH]. Ionization cross sections of atoms calculated by Mann [70MAN] were used to obtain the ionization cross section of LiOD molecule (the numerical value of LiOD cross section was not given). Activities of condensed phases were assumed to be unity. Four runs of measurements of varying  $\text{D}_2\text{O}$  pressure (0.13–0.51 Pa) were made in the temperature range 1188–1422 K. The variation of  $\text{D}_2\text{O}$  pressure produced no observable effect on the equilibrium. The values of the equilibrium constant, presented in a graph, were fitted by a least squares method to the expression (pressure was in Pa):

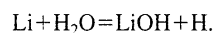
$$\log K^\circ = -10^3(24.43 \pm 0.73)T^{-1} + (15.76 \pm 0.56).$$

The error estimate represents a 95% confidence level. This equation yielded the value  $\Delta_f H^\circ(1305 \text{ K}) = 467.7 \pm 14 \text{ kJ mol}^{-1}$ . The value  $\Delta_f H^\circ(298.15 \text{ K}) = 469.2 \text{ kJ mol}^{-1}$  was given by [92PEN/IHL] as obtained by the third law treatment of equilibrium constant values using Gibbs energy functions from [85CHA/DAV]. The Gibbs energy functions for  $\text{Li}_4\text{SiO}_4(\text{cr})$  were not given in [85CHA/DAV], however.

Enthalpy of Formation of  $\text{LiOH}(\text{g})$ —*Ab initio* Calculations

[76CAR/ZAH]

Carsky, Zahradnik, and Kozák carried out *ab initio* SCF calculations (double zeta quality) for the gaseous reaction



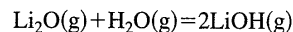
They obtained the enthalpy value  $\Delta_f H^\circ(0) = 9.40 \text{ kcal mol}^{-1}$  ( $39.3 \text{ kJ mol}^{-1}$ ). The corresponding enthalpy of formation is  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0) = -258 \text{ kJ mol}^{-1}$ .

[81TAM/SZA]

Tamássy-Lentei and Szaniszló carried out calculations for the  $\text{Li}^+ \text{-OH}^-$  system with the very simple FSGO (floating spherical Gaussian orbital) method. They obtained the value  $D_e(\text{Li}^+ \text{-OH}^-) = 0.341$  hartrees ( $895 \text{ kJ mol}^{-1}$ ). Applying the zero-point correction ( $7.9 \text{ kJ mol}^{-1}$ ), found using vibrational frequencies previously adopted, gives the value  $D_0(\text{Li}^+ \text{-OH}^-) = 887 \text{ kJ mol}^{-1}$ . This value corresponds to the enthalpy of formation  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0) = -342 \text{ kJ mol}^{-1}$ . The values  $\Delta_f H^\circ(\text{Li}^+, \text{g}, 0)$  and  $\Delta_f H^\circ(\text{OH}^-, \text{g}, 0)$  were taken from [82GUR/VEI] and [89GUR/VEI].

[82RAG]

Raghavachari performed an extensive theoretical study of the  $\text{H}_2\text{O-Li}_2\text{O}$  system by *ab initio* molecular orbital methods using several basis sets. Reaction energies were calculated with the 6-31G\*\*+sp basis; electron correlation was included by Möller–Plesset perturbation theory to third order. For the reaction



the calculated value of  $\Delta_f H^\circ(0)$  was found to be  $-20.9 \text{ kcal mol}^{-1}$  ( $-87.4 \text{ kJ mol}^{-1}$ ). A zero-point correction was applied in [82RAG] using frequencies calculated with the 3-21G basis set. The enthalpy of formation,  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0) = -246.4 \text{ kJ mol}^{-1}$ , corresponds to this value of enthalpy of reaction.

[84BAU]

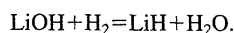
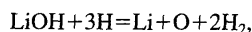
Bauschlicher obtained the value  $D_0(\text{Li-OH}) = 4.72 \pm 0.06 \text{ eV}$  ( $455 \pm 6 \text{ kJ mol}^{-1}$ ) from *ab initio* calculation for the  $\text{Li}^+ \text{-OH}^-$  system with inclusion of configuration interaction. The enthalpy of formation  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0) = -258 \pm 6 \text{ kJ mol}^{-1}$  corresponds to this value.

[86BAU/LAN]

Bauschlicher, Langhoff, and Partridge calculated dissociation energies of the alkali hydroxide molecules MOH into  $\text{M}^+$  and  $\text{OH}^-$  ions by *ab initio* methods at both the self-consistent-field (SCF) and singles plus doubles configuration-interaction level CI(SD) using extended Gaussian basis sets of at least triple-zeta plus double polarization quality. The following values of dissociation energy were obtained:  $D_e(\text{Li-OH}) = 4.75 \text{ eV}$  (SCF),  $D_e(\text{Li-OH}) = 4.74 \text{ eV}$  (CI(SD)). As the “best” was chosen the value  $D_0(\text{Li-OH}) = 4.64 \pm 0.10 \text{ eV}$  ( $448 \pm 10 \text{ kJ mol}^{-1}$ ) calculated with zero-point correction taken equal to 0.10 eV. The “best” value corresponds with the enthalpy of formation  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0) = -251 + 10 \text{ kJ mol}^{-1}$ .

[91SAN/LER]

Sana and Leroy [91SAN/LER] calculated the enthalpy of formation of LiOH molecules from the enthalpies of two reactions:



Calculations were performed with 6-31+G(2df,p) and 6-31+G(3df,2p) basis sets. Electron correlation was included using Møller–Plesset perturbation theory to fourth order. The  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0)$  values found were, correspondingly,  $-57.77 \text{ kcal mol}^{-1}$  ( $-241.7 \text{ kJ mol}^{-1}$ ) and  $-57.36 \text{ kcal mol}^{-1}$  ( $-240.0 \text{ kJ mol}^{-1}$ ).

[91CUR/RAG], see also [89POP/HEA]

Curtiss, Raghavachari, Trucks, and Pople, calculated the atomization energy of LiOH(g) using composite Gaussian-1 and Gaussian-2 *ab initio* theoretical procedures, utilizing large basis sets and treating electron correlation by Møller–Plesset perturbation theory and by quadratic configuration interaction. The Gaussian-2 procedure made a significant improvement over the Gaussian-1 theory. In particular, the Gaussian-2 theory produced better results for atomization energy of ionic molecules. For LiOH molecule following atomization enthalpies  $\Sigma D_0$  were obtained: Gaussian-1,  $207.4 \text{ kcal mol}^{-1}$  ( $867.8 \text{ kJ mol}^{-1}$ ); Gaussian-2,  $204.8 \text{ kcal mol}^{-1}$  ( $856.9 \text{ kJ mol}^{-1}$ ). Zero-point correction was applied in [91CUR/RAG] using scaled HF/6-31G\* harmonic frequencies (not listed in [91CUR/RAG]). The values given correspond to the following enthalpies of formation,  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0)$ : Gaussian-1,  $-247.2 \text{ kJ mol}^{-1}$ ; Gaussian-2,  $-236.3 \text{ kJ mol}^{-1}$  (calculated using enthalpies of formation for Li(g) from [82GUR/VEI] and for O(g) and H(g) from [89GUR/VEI]).

In addition, the total energy values presented in [91CUR/RAG] made it possible to calculate from these data dissociation energies  $D_0(\text{Li-OH})$  and  $D_0(\text{Li}^+ \text{-OH}^-)$ ,  $\text{kJ mol}^{-1}$ :

Gaussian-1,  $D_0(\text{Li-OH})=447.3$ ,  $D_0(\text{Li}^+ \text{-OH}^-)=784.8$ ;  
Gaussian-2,  $D_0(\text{Li-OH})=432.0$ ,  $D_0(\text{Li}^+ \text{-OH}^-)=766.8$ .

The following  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0)$  values ( $\text{kJ mol}^{-1}$ ) correspond to dissociation energies listed:

Gaussian-1,  $-250.5$  and  $-239.9$ , respectively;  
Gaussian-2,  $-235.2$  and  $-225.9$ , respectively.

#### Discussion of the Enthalpy of Formation of LiOH(g)

The authors of this review have recalculated all equilibrium constant values with the thermal functions from this work and auxiliary data from [82GUR/VEY] and [89GUR/VEY]. The recalculated values of enthalpies of reactions and the values of enthalpy of formation of LiOH(g) are collected in Table 2-17. For the enthalpies of reaction, results of the second-law and third-law treatment are presented; error assessments represent statistical uncertainty (95% confidence level). For the enthalpy of formation, the third-law values are given. Error assessments represent total uncertainty estimates, obtained on the basis of all error constituents (statistical uncertainty, estimate of systematic error in equilibrium constant values, uncertainty of thermal functions and auxiliary thermochemical data).

As can be seen in Table 2-17, the result of the first flame investigation [53SMI/SUG] strongly deviates from the most reliable flame photometric works ([66JEN/PAD], [69COT/JEN], [71KEL/PAD], [90BEL/LEB]) which are in good agreement. Smith and Sugden [53SMI/SUG] used, in their calculation of the equilibrium constant value, the hydroxyl partial pressure calculated assuming attainment of equilibrium in the burnt gases. McEwan and Phillips [67MCE/PHI] and Zeegers and Alkemade [70ZEE/ALK] came to the conclusion that, under Smith and Sugden's [53SMI/SUG] experimental conditions, radical concentrations were in excess of equilibrium values. This excess would make the  $D_0(\text{Li-OH})$  value, calculated by Smith and Sugden using equilibrium OH concentration, systematically too low. Correspondingly, the value of enthalpy of formation from the work by Smith and Sugden [53SMI/SUG] is more positive than the more reliable values from [66JEN/PAD], [69COT/JEN], [71KEL/PAD], and [90BEL/LEB]. In the papers [67MCE/PHI] and [70ZEE/ALK] no details were given concerning the data from the dissertations of Phillips [60PHI] and Zeegers [65ZEE]. For this reason, the values of  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0)$  from these papers were not taken into consideration in obtaining the recommended value.

The value of the enthalpy of formation of LiOH(g) from the work by Berkowitz, Meschi and Chupka [60BER/MES] lies  $\approx 13 \text{ kJ mol}^{-1}$  apart from the most reliable flame photometric data. The authors of this review believe that this discrepancy can be attributed to the choice of ratio of ionization cross section values for LiOH and  $\text{H}_2\text{O}$  molecules in [60BER/MES]. The value of this ratio was not presented in [60BER/MES]. Nevertheless, it can be derived from the mass spectrum of the  $\text{Li}_2\text{O}(\text{cr})\text{-H}_2\text{O}(\text{g})$  system ( $T=1350 \text{ K}$ ,  $P(\text{H}_2\text{O})=0.16 \text{ mm Hg}$ ) and the equilibrium constant value  $K^\circ=2.21 \times 10^{-4}$  for reaction (2) at the same temperature  $P(\text{LiOH})=2.157 \times 10^{-4} \text{ atm}$  ( $0.164 \text{ mm Hg}$ ). The comparison of ion intensities and partial pressure values gives the ratio of ionization cross sections for the formation of corresponding molecular ions:  $r = \sigma(\text{LiOH}^+/\text{LiOH})/\sigma(\text{H}_2\text{O}^+/\text{H}_2\text{O})=1.1$ . A common approach in evaluation of molecular ionization cross sections consists in using atomic ionization cross section calculated by Mann [70MAN] in combination with the additivity rule (or additivity rule with some modifications which make the total ionization cross section lower than the sum of atomic ones). From the point of view of the additivity rule, the value  $r=1.1$  seems to be too low, because the lithium ionization cross section is much higher than that of hydrogen.

We have calculated the  $r$ -value using the additivity rule. As the first step, the total ionization cross section ratio  $r_t$  was found using maximum values of atomic cross section from [70MAN]:  $r_t=2.8$ . The use of maximum cross section values is justified, because ion current measurements in [60BER/MES] were carried out at electron energy  $75 \text{ eV}$ , i.e., near

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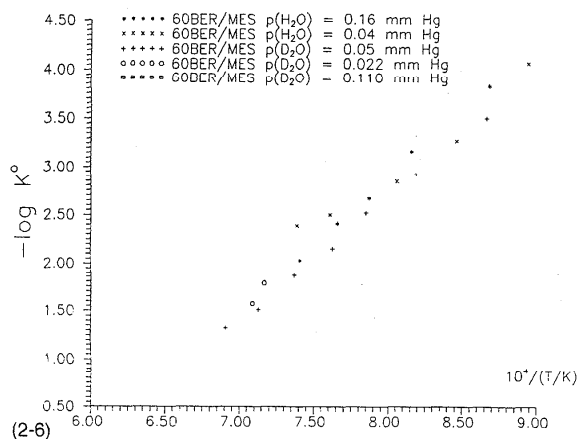
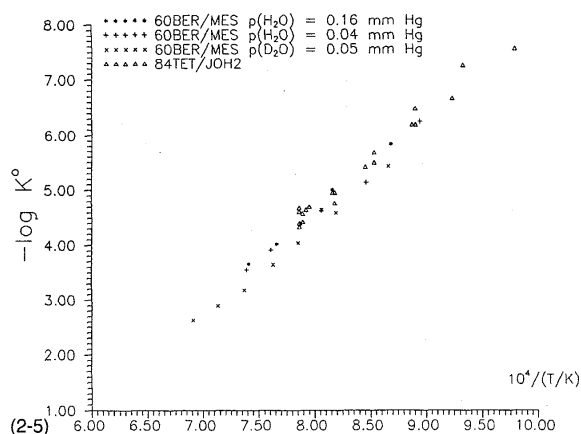
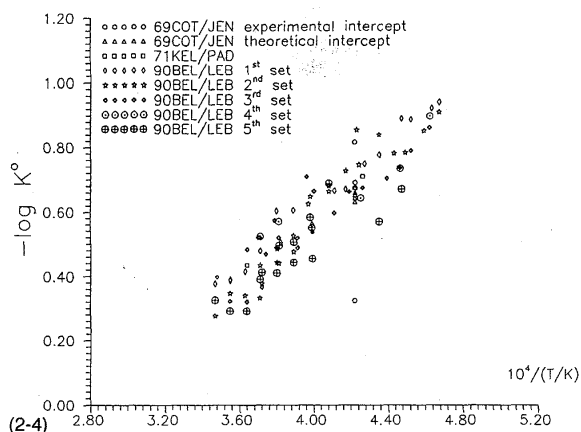


FIG. 2-4. Equilibrium constant values for reaction  $\text{Li}(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{LiOH}(\text{g}) + \text{H}(\text{g})$ .

(2-5) Equilibrium constant values for reaction  $\text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g}) = 2\text{LiOH}(\text{g})$ .

(2-6) Equilibrium constant values for reaction  $\text{Li}_2\text{O}_2\text{H}_2(\text{g}) = 2\text{LiOH}(\text{g})$ .

maxima of the ionization efficiency curves. The  $r$ -value was calculated taking into account the fragmentation of  $\text{LiOH}$  and  $\text{H}_2\text{O}$  molecules under electron impact:  $r=4.1$ . The data on fragmentation of  $\text{H}_2\text{O}$  molecules were taken from [66SCH/DEH]. From the above considerations, it follows that  $P(\text{LiOH})$  values in [60BER/MES] are to be multiplied by the correction factor of  $1.1:4.1 \approx 0.3$ , and all values of equilibrium constant for reaction (2) are to be multiplied by the correction factor of  $(0.3)^2 = 0.09$ . The average value of correction of enthalpy of reaction (2), corresponding to the mean temperature,  $\approx 1300$  K, is  $\delta(\Delta H^\circ) = -RT \ln 0.09 = 26.0$  kJ mol $^{-1}$ . The recalculated third-law value of the enthalpy of formation of  $\text{LiOH}(\text{g})$  with the total uncertainty estimate is:

$$\Delta_f H^\circ(\text{LiOH}, \text{g}, 0) = -227.2 \pm 8 \text{ kJ mol}^{-1}.$$

The recalculated value is in good agreement with the results of flame photometric studies. Results of Penzhorn *et al.* [92PEN/IHL] are also in good agreement with this value. The reliability of the latter work is lower, however, because large amounts of auxiliary information are necessary for the calculation of  $\Delta_f H^\circ(\text{LiOH}, \text{g}, 0)$  from the data of [92PEN/IHL] (thermal functions and enthalpies of formation for  $\text{Li}_2\text{SiO}_3(\text{cr})$  and  $\text{Li}_4\text{SiO}_4(\text{cr})$  were taken from [85CHA/DAV] and [77BAR/KNA], respectively).

The work of Tetenbaum and Johnson [84TET/JOH2] was carried out using a variation of transpiration techniques, capable of producing reliable data if measurements were made in the plateau region, where results of vapor pressure or equilibrium constant calculations are independent of carrier gas flow rate. No direct evidence of working in the plateau region was given in [84TET/JOH2]. In previous works of Tetenbaum *et al.*, results independent of flow rate were obtained in the ranges of 80–200 cm $^3$  min $^{-1}$  and 50–150 cm $^3$  min $^{-1}$  (see [70TET/HUN] and [84TET/JOH]). In [84TET/JOH2], the range of flow rates was more broad, e.g., four measurements were made at the temperature  $T=1273$  K at the following flow rates: 16, 48, 161, and 248 cm $^3$  min $^{-1}$ . The third-law values of the enthalpy of reaction (2) show systematic drift from 361.0 to 352.4 kJ mol $^{-1}$  with decreasing flow rate. These results possibly indicate the influence of  $\text{LiOH}(\text{g})$  diffusion at low flow rates of carrier gas. The diffusion was probably enhanced because of using helium as carrier gas. Difficulties in transpiration measurements with  $\text{Li}_2\text{O}(\text{cr})\text{-H}_2\text{O}(\text{g})$  system were revealed also in the work [63BER/BUE]. The above considerations cast some doubt on the reliability of the data obtained in [84TET/JOH2].

Results of quantum-mechanical *ab initio* calculations are collected in Table 2-18. Early calculation of  $\text{LiOH}$  dissociation energy of modest level [81TAM/SZA] gave results far from experimental values. In the case of exchange reactions ([76CAR/ZA], [82RAG], [91SAN/LER]), calculations gave enthalpies of formation in more reasonable agreement with those calculated from experimental equilibrium constant values, due to partial compensation of basis set and correlation effects. Comparison of the results obtained in

[76CAR/ZAH], [82RAG], and [91SAN/LER] shows that higher level computations result in more positive enthalpy of formation values. The same trend is noticeable by comparison of direct calculations of LiOH dissociation energy. The latest and the most advanced procedure, Gaussian-2 ([91CUR/RAG]), leads to  $\Delta_f H^\circ(\text{LiOH,g,0})$  values, which were very close to those obtained in the most reliable flame-photometric work [90BEL/LEB].

On the basis of the above discussion we adopt the value

$$\Delta_f H^\circ(\text{LiOH,g,298.15 K}) = -229.0 \pm 5 \text{ kJ mol}^{-1}.$$

This value is calculated as a slightly rounded weighted average of the data from the works [60BER/MES] (as corrected), [66JEN/PAD], [69COT/JEN], [71KEL/PAD], and [90BEL/LEB]. Comparison of the adopted value with the values from major reviews is given in Table 2-19.

## 2.2.2. Appendix. Tables of Experimental and Evaluated Data for LiOH(g)

TABLE 2-15. Equilibrium constant values for  $\text{Li(g)} + \text{H}_2\text{O(g)} = \text{LiOH(g)} + \text{H(g)}$ .

1. [69COT/JEN]								
N	T/K	$K^\circ(T)^a$	N	T/K	$K^\circ(T)^b$			
1	2370	0.212	1	2370	0.254			
2	2370	0.212	2	2370	0.267			
3	2370	0.204	3	2370	0.281			
4	2370	0.153	4	2370	0.263			
5	2370	0.474	5	2370	0.274			
2. [90BEL/LEB]								
First set			Second set			Third set		
N	T/K	$K^\circ(T)$	N	T/K	$K^\circ(T)$	N	T/K	$K^\circ(T)$
1	2160	0.120	1	2180	0.141	1	2165	0.138
2	2239	0.129	2	2259	0.166	2	2244	0.184
3	2341	0.179	3	2360	0.180	3	2345	0.212
4	2433	0.216	4	2450	0.217	4	2436	0.253
5	2506	0.275	5	2522	0.237	5	2508	0.290
6	2617	0.312	6	2629	0.324	6	2671	0.340
7	2698	0.332	7	2629	0.326	7	2690	0.431
8	2756	0.384	8	2698	0.367	8	2751	0.477
9	2214	0.130	9	2756	0.456	9	2212	0.163
10	2298	0.168	10	2227	0.165	10	2284	0.198
11	2400	0.214	11	2298	0.145	11	2385	0.218
12	2818	0.406	12	2400	0.188	12	2816	0.475
13	2143	0.115	13	2818	0.449	13	2725	0.117
14	2567	0.248	14	2143	0.123	14	2498	0.217
15	2629	0.249	15	2364	0.140	15	2524	0.196
16	2880	0.420	16	2450	0.208	16	2558	0.324
17	2818	0.410	17	2502	0.287	17	2625	0.302
			18	2513	0.225	18	2638	0.267
			19	2567	0.333	19	2694	0.302
			20	2629	0.360	20	2704	0.302
			21	2626	0.361	21	2751	0.328
			22	2690	0.418	22	2876	0.400
			23	2694	0.464	23	2558	0.303
			24	2880	0.528			
			25	2567	0.297			
Fourth set			Fifth set					
N	T/K	$K^\circ(T)$	N	T/K	$K^\circ(T)$			
1	2165	0.127	1	2239	0.214			
2	2244	0.185	2	2506	0.351			
3	2355	0.228	3	2698	0.406			
4	2625	0.269	4	2298	0.269			
5	2694	0.300	5	2818	0.510			
			6	2450	0.205			
			7	2502	0.281			
			8	2513	0.216			
			9	2567	0.360			
			10	2629	0.388			
			11	2626	0.319			
			12	2690	0.386			
			13	2880	0.472			
			14	2567	0.311			
			15	2749	0.511			

<sup>a</sup>Calculated from the slope intercept values obtained through least squares treatment of experimental data (see the text).

<sup>b</sup>Calculated from the slope intercept values using theoretical value of the intercept (see the text).

TABLE 2-16. Equilibrium constant values for  $\text{Li}_2\text{O} + \text{H}_2\text{O}(\text{g}) = 2\text{LiOH}(\text{g})$ .

1. [60BER/MES]			2. [84TET/JOH2]		
N	T/K	$K^\circ(T)$	N	T/K	$K^\circ(T)$
1	1350	$2.21 \times 10^{-4}$	1	1073	-7.25
2	1306	$9.73 \times 10^{-5}$	2	1123	-6.48
3	1270	$4.14 \times 10^{-5}$	3	1123	-6.19
4	1226	$1.0 \times 10^{-5}$	4	1128	-6.19
5	1152	$1.48 \times 10^{-6}$	5	1173	-5.49
6	1119	$5.70 \times 10^{-7}$	6	1183	-5.41
7	1241	$2.37 \times 10^{-5}$	7	1223	-4.76
8	1314	$1.25 \times 10^{-4}$	8	1226	-4.95
9	1182	$7.32 \times 10^{-6}$	9	1258	-4.70
10	1352	$2.83 \times 10^{-4}$	10	1263	-4.64
11	1154	$3.78 \times 10^{-6}$	11	1268	-4.42
12	1221	$2.60 \times 10^{-5}$	12	1268	-4.57
13	1274	$9.21 \times 10^{-5}$	13	1223	-4.95
14	1310	$2.29 \times 10^{-4}$	14	1023	-7.55
15	1357	$6.61 \times 10^{-4}$	15	1273	-4.40
16	1403	$1.30 \times 10^{-3}$	16	1273	-4.61
17	1448	$2.38 \times 10^{-3}$	17	1273	-4.68
18	1240	$2.3 \times 10^{-5}$	18	1273	-4.33
			19	1173	-5.67
			20	1083	-6.66

TABLE 2-17. Results of experimental determinations of  $\Delta_f H^\circ$  (LiOH,g,0), kJ mol<sup>-1</sup>.

Reference	Method	$\Delta_f H^\circ(0)$		$\Delta_f H^\circ(0)$ Third law
		Second law	Third law	
1. Equilibria in flames				
[53SM/SUG]	Measurements of electron concentration in $\text{H}_2$ +air flames, $\text{LiOH}(\text{g}) = \text{Li}(\text{g}) + \text{OH}(\text{g})$ , 2200 K (1 point)	...	$\geq 406$	$\leq -209$
[60PHI]	Atomic absorption flame photometry, $\text{Li}(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{LiOH}(\text{g}) + \text{H}(\text{g})$ , 2600 K (1 point; experimental details are not given)	...	$78 \pm 10$	$-219 \pm 10$
[66JEN/PAD]	Atomic absorption flame photometry, $\text{Li}(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{LiOH}(\text{g}) + \text{H}(\text{g})$ , $\text{H}_2 + \text{O}_2 + \text{N}_2$ flame, 2475 K (1 point)	...	72.4	$-224.8 \pm 5$
[65ZEE]	$\text{LiOH}(\text{g}) = \text{Li}(\text{g}) + \text{OH}(\text{g})$ , (experimental details are not given)	$440.6 \pm 8$	$448 \pm 8$	$-251 \pm 10$
[70ZEE/ALK]	Atomic absorption flame photometry, $\text{Li}(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{LiOH}(\text{g}) + \text{H}(\text{g})$ , a set of 5 ( $\text{H}_2 + \text{N}_2 + \text{O}_2$ ) isothermal flames, 2370 K (5 points)	...	$69.0 \pm 1.0$	$-228.3 \pm 5$
[71KEL/PAD]	Atomic emission flame photometry, $\text{Li}(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{LiOH}(\text{g}) + \text{H}(\text{g})$ , ( $\text{H}_2 + \text{CO}_2 + \text{O}_2$ ) and ( $\text{H}_2 + \text{N}_2 + \text{O}_2$ ) flames, 1950-2750 K (33 points)	62.4	$70.9 \pm 2.3$	$-226.2 \pm 5$
[90BEL/LEB]	Atomic absorption flame photometry, $\text{Li}(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{LiOH}(\text{g}) + \text{H}(\text{g})$ , natural gas+air+O, 2143-2880 K (85 points)	$69.7 \pm 8$	$69.7 \pm 0.8$	$-227.3 \pm 5$
2. Solid-gas equilibria				
[60BER/MES]	Knudsen effusion mass spectrometry, $\text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g}) = 2\text{LiOH}(\text{g})$ , 1119-1448 K (18 points)	$341.5 \pm 29$	$350.0 \pm 2$	$-240.2 \pm 8$ $-227.2 \pm 8^*$
[84TET/JOH2]	Transpiration, $\text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g}) = 2\text{LiOH}(\text{g})$ , 1023-1273 K (20 points)	$319.4 \pm 22$	$354.0 \pm 1.8$	$-238.3 \pm 7$
[92PEN/IHL]	Knudsen effusion mass spectrometry, $\text{Li}_2\text{SiO}_4(\text{cr}) + \text{D}_2\text{O}(\text{g}) = \text{Li}_2\text{SiO}_4(\text{cr}) + 2\text{LiOD}(\text{g})$ , 1118-1422 K; the data are presented in the form of an equation (20 points)	$450.3 \pm 14$ (T=298.15 K)	$477.8 \pm 4.1$ (T=298.15 K)	$-220.4 \pm 15$

\*Recalculated (see the text).

TABLE 2-18. Results of quantum-mechanical calculations of  $\Delta_f H^\circ$  (LiOH,g,0).

Reference	$\Delta_f H^\circ$ (LiOH,g,0) kJ mol <sup>-1</sup>
[76CAR/ZA]	-258
[81TAM/SZA]	-342
[82RAG]	-246.4
[84BAU]	-258±6
[86BAU/LAN]	-251±10
[91SAN/LER]	-241.7 <sup>a</sup> -240.0 <sup>b</sup>
[91COR/HEA]	-236.3 <sup>c</sup> -235.2 <sup>d</sup> -225.9 <sup>e</sup>

<sup>a</sup>Reaction LiOH+3H=Li+O+2H<sub>2</sub>.<sup>b</sup>Reaction LiOH+H<sub>2</sub>+LiH+H<sub>2</sub>O.<sup>c</sup>From  $\Sigma D_0$ , Gaussian-2 (see the text).<sup>d</sup>From  $D_0$  (Li-OH), Gaussian-2.<sup>e</sup>From  $D_0$  (Li<sup>+</sup> OH<sup>-</sup>), Gaussian-2.

TABLE 2-19. Comparison of the heat capacity, enthalpy, entropy, and enthalpy of formation values for LiOH(g).

Reference	$C_p^\circ$ (298.15 K)	$S^\circ$ (298.15 K)	$H^\circ(298.15 \text{ K}) - H^\circ(0)$	$\Delta_f H^\circ$ (298.15 K)
	J K <sup>-1</sup> mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>
82MED/BER	44.4	209.2	10.63	-241.1±12
82WAG/EVA	46.02	210.90	10.908	-238.1
82GUR/VEY	44.328	209.463	10.631	-245.576±8
85CHA/DAV	46.129	210.659	10.879	-234.3±6.3
Adopted	46.026	214.375	11.337	-229.0±5

TABLE 2-20. Thermodynamic properties at 0.1 MPa: LiOH(g).

T(K)	$C_p^\circ$	$-(G^\circ - H^\circ(0))T^{-1}$	$S^\circ$	$H^\circ - H^\circ(0)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
	J (mol K) <sup>-1</sup>			kJ mol <sup>-1</sup>		
0	0.000	0.000	0.000	0.000	-227.131	-227.131
25	29.103	98.573	127.481	0.723	-227.038	-227.867
50	29.666	118.658	147.740	1.454	-227.142	-228.677
75	32.081	130.537	160.175	2.223	-227.339	-229.401
100	35.052	139.191	169.816	3.062	-227.513	-230.060
150	39.515	152.041	184.947	4.936	-227.836	-231.263
200	42.342	161.793	196.727	6.987	-228.235	-232.320
250	44.424	169.777	206.409	9.158	-228.618	-233.298
300	46.081	176.586	214.660	11.422	-229.015	-234.202
350	47.417	182.551	221.867	13.761	-229.405	-235.037
400	48.493	187.873	228.272	16.159	-229.819	-235.813
450	49.362	192.687	234.035	18.607	-230.289	-236.534
500	50.071	197.088	239.274	21.093	-233.814	-236.894
600	51.164	204.909	248.505	26.158	-234.774	-237.418
700	52.005	211.718	256.457	31.318	-235.651	-237.789
800	52.727	217.756	263.450	36.553	-236.472	-238.038
900	53.392	223.186	269.699	41.861	-237.250	-238.186
1000	54.023	228.125	275.357	47.232	-237.995	-238.250
1100	54.627	232.658	280.534	52.665	-238.715	-238.242
1200	55.199	236.849	285.312	58.156	-239.419	-238.167
1300	55.738	240.750	289.752	63.703	-240.113	-238.034
1400	56.240	244.400	293.901	69.303	-240.805	-237.850
1500	56.705	247.831	297.798	74.950	-241.505	-237.614
1600	57.132	251.070	301.471	80.642	-242.221	-237.330
1700	57.523	254.138	304.947	86.375	-242.807	-237.992
1800	57.880	257.053	308.245	92.146	-243.262	-237.613
1900	58.205	259.830	311.383	97.950	-243.598	-237.194
2000	58.501	262.483	314.376	103.786	-243.815	-236.744
2200	59.017	267.459	319.977	115.539	-244.001	-236.186
2400	59.444	272.053	325.131	127.387	-244.162	-235.613
2600	59.801	276.322	329.904	139.312	-244.299	-235.034
2800	60.100	280.310	334.347	151.303	-244.405	-234.449
3000	60.352	284.052	338.502	163.349	-244.482	-233.858
3200	60.566	287.578	342.404	175.441	-244.530	-233.262
3400	60.749	290.913	346.081	187.573	-244.558	-232.662
3600	60.906	294.075	349.558	199.739	-244.567	-232.058
3800	61.042	297.083	352.855	211.934	-244.557	-231.451
4000	61.160	299.950	355.989	224.155	-244.528	-230.841
4200	61.264	302.691	358.976	236.397	-244.480	-230.228
4400	61.355	305.314	361.828	248.659	-244.414	-229.613
4600	61.435	307.831	364.557	260.939	-244.330	-228.997
4800	61.506	310.250	367.173	273.233	-244.229	-228.380
5000	61.570	312.577	369.685	285.540	-244.113	-227.762
5200	61.626	314.820	372.101	297.860	-244.000	-227.142
5400	61.677	316.985	374.428	310.190	-243.881	-226.520
5600	61.723	319.077	376.672	322.531	-243.758	-225.897
5800	61.765	321.101	378.838	334.879	-243.632	-225.272
6000	61.802	323.060	380.933	347.236	-243.503	-224.647
298.150	46.026	176.351	214.375	11.337	-229.000	-234.171

## Uncertainties in Functions

0	0.000	0.000	0.000	0.000	0.000	0.000
298.15	0.500	0.700	1.200	0.150	5.000	5.000
1000	0.800	1.000	1.400	0.400	5.000	5.000
2000	1.000	1.200	1.600	0.800	5.000	5.000
3000	1.200	1.500	1.800	1.000	6.000	5.000
4000	1.500	1.800	2.200	1.500	6.000	7.000
5000	1.800	2.100	2.600	2.000	6.000	10.000
6000	2.000	2.500	3.000	2.500	6.000	14.000

## 2.2.3. Lithium Hydroxide Dimer

Molecular constants of  $\text{Li}_2\text{O}_2\text{H}_2$ 

[60BER/MES]

Berkowitz *et al.*, in the course of an experimental study of the reaction of water vapor with lithium oxide, estimated the molecular constants of  $\text{Li}_2\text{O}_2\text{H}_2$ . They assumed  $C_{2h}$  symmetry with a planar rhomboid  $\text{Li}_2\text{O}_2$  skeleton and the out-of-plane *trans* orientation of the H atoms. The structural parameters and vibrational frequencies of  $\text{Li}_2\text{O}_2\text{H}_2$  were estimated by comparison with  $\text{Li}_2\text{F}_2$  and  $\text{H}_2\text{O}$ .

[63MCB/HEI]

McBride *et al.* estimated the molecular constants of the  $\text{Li}_2\text{O}_2\text{H}_2$  molecule assuming  $D_{2h}$  symmetry.

[82GUR/VEY]

Gurvich *et al.* estimated the molecular constants of the  $\text{Li}_2\text{O}_2\text{H}_2$  molecule by comparison with similar molecules (the other alkali hydroxide dimers and the alkali fluoride dimers) assuming  $D_{2h}$  symmetry.

[82RAG]

Raghavachari investigated the  $\text{H}_2\text{O-Li}_2\text{O}$  system by *ab initio* methods with the 3-21G and 6-31G\* basis sets. Electron correlation was included by using the Møller-Plesset perturbation theory up to the third order. The harmonic frequencies of the  $\text{Li}_2\text{O}_2\text{H}_2$  molecule were calculated using the 3-21G basis set; for calculation of the geometry, a larger set, 6-31G\*, was used.

[83SOL/POG] (see also [83SOL], [83SOL/POG2], [90POG])

Solomonik with co-workers performed *ab initio* calculations for the  $\text{Li}_2\text{O}_2\text{H}_2$  molecule using the MO LCAO SCF method. The geometry and harmonic frequencies were obtained with the basis set Li 9s4p/4s2p, O 9s5p/4s2p and H4s1p/2s1p.

[85CHA/DAV]

Chase *et al.* assumed that the molecular configuration of  $\text{Li}_2\text{O}_2\text{H}_2$  consisted of a square planar  $\text{Li}_2\text{O}_2$  skeleton with the hydrogen atoms in *trans*-positions above and below the plane ( $C_{2h}$  symmetry). The structural parameters were estimated. The six vibrational frequencies belonging to the  $\text{Li}_2\text{O}_2$  skeleton were estimated by comparison with corresponding frequencies of  $\text{Li}_2\text{F}_2$  assuming that the OH group would tend to reduce the frequencies of  $\text{Li}_2\text{O}_2\text{H}_2$ . The remaining OH frequencies were taken from [60BER/MES] (Table 2-20).

Discussion of the Molecular Constants of  $\text{Li}_2\text{O}_2\text{H}_2$ 

The lithium hydroxide dimer is known only as a component of high-temperature equilibrium. Its structure and vibrational frequencies were not studied experimentally. In the earlier publication by Berkowitz *et al.*, a  $C_{2h}$  configuration was assumed for  $\text{Li}_2\text{O}_2\text{H}_2$  with planar  $\text{Li}_2\text{O}_2$  rhomboid part and *trans*-position of the H atoms above and below the plane. A similar configuration was chosen in [63MCB/HEI] and in JANAF Thermochemical Tables [85CHA/DAV] but with a square planar  $\text{Li}_2\text{O}_2$  skeleton. The estimation of the

molecular constants in all cases was made by comparison with the lithium fluoride dimer and the water molecule. In [82GUR/VEY], a  $D_{2h}$  configuration for  $\text{Li}_2\text{O}_2\text{H}_2$  was accepted (planar molecule with rhomboid  $\text{Li}_2\text{O}_2$  part and H atoms on the O-O line) by analogy with higher alkali metal hydroxide dimers for which such a configuration was determined experimentally. All molecular constants were estimated. The  $D_{2h}$  configuration of the  $\text{Li}_2\text{O}_2\text{H}_2$  molecule was confirmed by Raghavachari [82RAG] and Solomonik [83SOL] who carried out *ab initio* calculations. In the calculation [82RAG], several possible configurations were tried, and it was shown that the most stable is  $D_{2h}$  configuration. The molecular constants of  $\text{Li}_2\text{O}_2\text{H}_2$  obtained in both *ab initio* studies are rather close to each other.

The molecular constants of  $\text{Li}_2\text{O}_2\text{H}_2$  reported in the literature are presented in Table 2-21. The following description of the vibration modes is used in the table:

$\nu_1$ ( $A_g$ )	-O-H stretching;
$\nu_2$ ( $A_g$ )	-Li-O stretching;
$\nu_3$ ( $A_g$ )	-in-plane ring deformation;
$\nu_4$ ( $B_{1g}$ )	-in-plane O-H bending;
$\nu_5$ ( $B_{1g}$ )	-Li-O stretching;
$\nu_6$ ( $B_{1u}$ )	-out-of-plane O-H bending;
$\nu_7$ ( $B_{1u}$ )	-out-of-plane ring deformation;
$\nu_8$ ( $B_{2g}$ )	-out-of-plane O-H bending;
$\nu_9$ ( $B_{2u}$ )	-in-plane O-H bending;
$\nu_{10}$ ( $B_{2u}$ )	-Li-O stretching;
$\nu_{11}$ ( $B_{3u}$ )	-O-H stretching;
$\nu_{12}$ ( $B_{3u}$ )	-Li-O stretching.

The molecular constants of  $\text{Li}_2\text{O}_2\text{H}_2$  used for calculation of the thermal functions are taken from the Raghavachari's [82RAG] *ab initio* calculation. The constants reported by Solomonik [83SOL] are close to those accepted in the present work, especially for the structural parameters, but the approach used in [82RAG] seems to be more precise. The estimated uncertainties are  $\pm 0.02 \text{ \AA}$  in  $r(\text{Li-O})$  and  $r(\text{O-H})$  and  $\pm 3^\circ$  in  $\angle(\text{O-Li-O})$ . The corresponding value of the product of the principal moments of inertia,  $I_A I_B I_C = (520 \pm 50)^{-117} \text{ g}^3 \text{ cm}^6$ , is accepted in the present work. The uncertainty in all accepted fundamental frequencies is 10%. The existence of low-lying excited electronic states of  $\text{Li}_2\text{O}_2\text{H}_2$  is not expected.

For  $\text{Li}_2\text{O}_2\text{H}_2$ , the symmetry number  $\sigma = 4$ , and statistical weight of the ground electronic state  $p_X = 1$ .

The molecular constants of  $\text{Li}_2\text{O}_2\text{H}_2$ , accepted in the present work for calculation of thermal functions, are summarized below:

$$\begin{aligned}
 r(\text{Li-O}) &= 1.781 \pm 0.02 \text{ \AA}; \\
 r(\text{O-H}) &= 0.941 \pm 0.02 \text{ \AA}; \\
 \angle(\text{O-Li-O}) &= 101 \pm 3^\circ; \\
 I_A I_B I_C &= (520 \pm 50) 10^{-117} \text{ g}^3 \text{ cm}^6; \\
 \sigma &= 4; \\
 p_X &= 1; \\
 \nu_1 &= 3968 \pm 300 \text{ cm}^{-1}, d_1 = 1; \\
 \nu_2 &= 774 \pm 75 \text{ cm}^{-1}, d_2 = 1;
 \end{aligned}$$

TABLE 2-21. Bond lengths (Å), angles (deg) and vibrational frequencies (cm<sup>-1</sup>) of Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub> in the ground electronic state.

Constants	[60BER/MES] <sup>a</sup>	[82GUR/VEY] <sup>a</sup>	[82RAG] <sup>b</sup>	[83SOL] <sup>c</sup>	[85CHA/DAV] <sup>a</sup>
r(Li-O)	1.90	1.78	1.781	1.784	1.74
r(O-H)		0.97	0.941	0.943	0.97
<(O-Li-O)	100	100	101	101.5	90
<i>trans</i> out-of-plane <(Li-O-H)		0	0	0	110
ν <sub>1</sub>	3700	3700	3968	4215	3700
ν <sub>2</sub>	465	700	774	683	500
ν <sub>3</sub>	441	450	438	398	400
ν <sub>4</sub>	1250	320	793	728	1250
ν <sub>5</sub>	418	440	573	526	450
ν <sub>6</sub>	1250	310	388	483	1250
ν <sub>7</sub>	365	300	272	289	350
ν <sub>8</sub>	1250	310	287	428	1250
ν <sub>9</sub>	1250	310	665	642	1250
ν <sub>10</sub>	385	520	649	565	400
ν <sub>11</sub>	3700	3700	3968	4215	3700
ν <sub>12</sub>	407	670	855	745	500
Symmetry	C <sub>2h</sub>	D <sub>2h</sub>	D <sub>2h</sub>	D <sub>2h</sub>	C <sub>2h</sub>

<sup>a</sup>Estimated.<sup>b</sup>Ab initio calculation; accepted in the present work.<sup>c</sup>Ab initio calculation.

$$\begin{aligned} \nu_3 &= 438 \pm 40 \text{ cm}^{-1}, d_3 = 1; \\ \nu_4 &= 793 \pm 80 \text{ cm}^{-1}, d_4 = 1; \\ \nu_5 &= 573 \pm 55 \text{ cm}^{-1}, d_5 = 1; \\ \nu_6 &= 388 \pm 35 \text{ cm}^{-1}, d_6 = 1; \\ \nu_7 &= 272 \pm 25 \text{ cm}^{-1}, d_7 = 1; \\ \nu_8 &= 287 \pm 25 \text{ cm}^{-1}, d_8 = 1; \\ \nu_9 &= 665 \pm 65 \text{ cm}^{-1}, d_9 = 1; \\ \nu_{10} &= 649 \pm 65 \text{ cm}^{-1}, d_{10} = 1; \\ \nu_{11} &= 3967 \pm 300 \text{ cm}^{-1}, d_{11} = 1; \\ \nu_{12} &= 573 \pm 55 \text{ cm}^{-1}, d_{12} = 1. \end{aligned}$$

**Calculation of the Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g) Thermal Functions**

The thermal functions of Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g) in the standard state are calculated in the "rigid rotor-harmonic oscillator" approximation with low-temperature quantum corrections according to the equations given in [89GUR/VEY]. The calculated values of  $C_p^\circ(T)$ ,  $\Phi^\circ(T)$ ,  $S^\circ(T)$ ,  $H^\circ(T) - H^\circ(0)$  at the temperature range 0–6000 K are given in Table 2-27.

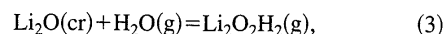
For Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g), all molecular constants are calculated theoretically and this is the principal source of the uncertainties in the thermal functions. Similar to LiOH, at higher temperatures the uncertainties due to the approximate method of calculation become more substantial. The total uncertainties in the thermal functions of Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g) are presented in Table 2-27.

The thermal functions of Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g) were calculated earlier in [60BER/MES] (500–2200 K), [63MCB/HEI] (298.15–6000 K), [82GUR/VEY] (100–6000 K), [83SOL] (298.15–3000 K), and [85CHA/DAV] (100–6000 K). The use of more reliable data in the present work results in differences of the thermal functions from those recommended

in earlier reviews. The comparison of the thermal functions for Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g) is shown in Table 2-22.

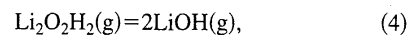
**Enthalpy of Formation of Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g)—Experimental Determinations [60BER/MES]**

In the mass spectrometric investigation of the Li<sub>2</sub>O(cr)-H<sub>2</sub>O(g) and Li<sub>2</sub>O(cr)-D<sub>2</sub>O(g) systems, Berkowitz, Meschi and Chupka have measured monomer and dimer ion intensities vs temperature (LiOH<sup>+</sup> and Li<sub>2</sub>OH<sup>+</sup> in the first and LiOD<sup>+</sup> and Li<sub>2</sub>OD<sup>+</sup> in the second system). From these data the authors [60BER/MES] calculated equilibrium constant values and enthalpies of reactions (3) and (4) (differences between hydrogen- and deuterium-bearing molecules were assumed to be insignificant; exact meaning of uncertainties was not specified):



$$\begin{aligned} \text{second law, } \Delta_r H^\circ(1250) &= 14 \pm 2 \text{ kcal mol}^{-1} \\ &= (58.6 \pm 8.4 \text{ kJ mol}^{-1}); \end{aligned}$$

$$\begin{aligned} \text{third law, } \Delta_r H^\circ(1300) &= 16 \pm 4 \text{ kcal mol}^{-1} \\ &= (66.9 \pm 17 \text{ kJ mol}^{-1}); \end{aligned}$$



$$\begin{aligned} \text{second law, } \Delta_r H^\circ(1300) &= 58 \pm 3 \text{ kcal mol}^{-1} \\ &= (242.7 \pm 13 \text{ kJ mol}^{-1}); \end{aligned}$$

$$\begin{aligned} \text{third law, } \Delta_r H^\circ(1300) &= 64 \pm 4 \text{ kcal mol}^{-1} \\ &= (267.8 \pm 17 \text{ kJ mol}^{-1}). \end{aligned}$$

In the third-law calculations a model of the Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub> molecule with a rhomboid structure of Li<sub>2</sub>O<sub>2</sub> fragment analo-

TABLE 2-22. Differences (in  $\text{J K}^{-1} \text{mol}^{-1}$ ) between the thermal functions of  $\text{Li}_2\text{O}_2\text{H}_2(\text{g})$  calculated in the present work and in [82GUR/VEY, 85CHA/DAV].

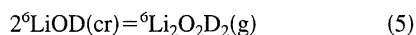
T, K	Present work-[82GUR/VEY] <sup>a</sup>			Present work-[85CHA/DAV] <sup>b</sup>		
	$\Delta C_p^\circ(T)$	$\Delta \Phi^\circ(T)$	$\Delta S^\circ(T)$	$\Delta C_p^\circ(T)$	$\Delta \Phi^\circ(T)$	$\Delta S^\circ(T)$
289.15	-11.695	-4.629	-12.258	8.662	-2.684	0.927
1000	-2.584	-13.870	-19.961	3.806	4.404	10.686
2000	-1.271	-17.313	-21.257	0.548	7.988	11.948
3000	-0.718	-18.704	-21.654	0.112	9.333	12.063
4000	-0.444	-19.465	-21.819	0.025	10.028	12.080
5000	-0.297	-19.941	-21.896	0.005	10.424	12.086
6000	-0.211	-20.271	-21.942	-0.001	10.710	12.085

<sup>a</sup>The values of  $\Phi^\circ(T)$  and  $S^\circ(T)$  tabulated in [82GUR/VEY] are recalculated to standard pressure 0.1 MPa.

<sup>b</sup>The values of  $\Phi^\circ(T)$  tabulated in [85CHA/DAV] are adjusted to the reference temperature  $T=0$  from 298.15 K.

gous to lithium halide dimers was used. The equilibrium constant values for reaction (4) are listed in Table 2-23 and are presented in Fig. 2-6.

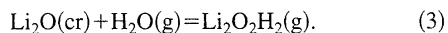
Two values of the equilibrium constant were obtained for the reaction



for the temperatures 598.0 K and 559.5 K:  $5.99 \times 10^{-9}$  and  $5.18 \times 10^{-9}$ , respectively. The values of  $\Delta_r H^\circ(T)$  for this reaction, calculated in the paper [60BER/MES] by the third law treatment of data, are 45.90 and 43.55  $\text{kcal mol}^{-1}$  (192.0 and 182.2  $\text{kJ mol}^{-1}$ ), respectively.

[63BER/BUE]

Berkowitz-Mattuck and Buechler carried out a transpiration study of lithium oxide in the presence of water vapor. The experiments were made at temperatures of 1095 K and 1145 K, with water vapor pressure of 4.58 mm Hg and 19.5 mm Hg. The carrier gas was dry  $\text{CO}_2$ -free argon. The flow rate of carrier gas was in the range from several  $\text{ml min}^{-1}$  to  $\approx 140 \text{ ml min}^{-1}$ . Analysis of the plot of experimental data in terms of weight loss vs flow rate led the authors [63BER/BUE] to the conclusion that "the range of flow rates for which diffusion is significant overlaps the region of under-saturated vapor." From the data of Berkowitz *et al.* [60BER/MES], Berkowitz-Mattuck and Buechler concluded that, at the water vapor pressures of 4.58 mm Hg and 19.5 mm Hg, evaporation of lithium hydroxide proceeds mainly in the form of  $\text{Li}_2\text{O}_2\text{H}_2$  molecules. They performed an analysis of the data taking into consideration kinetics of diffusion and saturation and obtained the values of equilibrium constant  $K^\circ(1095)=0.105$  and  $K^\circ(1145)=0.357$  for the reaction



The values of the enthalpy of formation were calculated in [63BER/BUE] using  $\text{Li}_2\text{O}_2\text{H}_2$  molecular parameters from the paper [60BER/MES]:

$T=1095 \text{ K}$ :  $\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0) = -183.6 \text{ kcal mol}^{-1}$  ( $-768.2 \text{ kJ mol}^{-1}$ );

$T=1145 \text{ K}$ :  $\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0) = -186.1 \text{ kcal mol}^{-1}$  ( $-778.6 \text{ kJ mol}^{-1}$ ).

#### Enthalpy of Formation of $\text{Li}_2\text{O}_2\text{H}_2$ —*Ab initio* Calculations [82RAG]

Raghavachari performed an extensive theoretical study of the  $\text{Li}_2\text{O}-\text{H}_2\text{O}$  system by *ab initio* molecular orbital methods using several basis sets. Reaction energies were calculated with the 6-31G\*\*+sp basis; electron correlation was included by Møller-Plesset perturbation theory to third order. The following enthalpy changes were obtained for gaseous reactions involving the  $\text{Li}_2\text{O}_2\text{H}_2$  molecule:

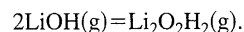
$\text{H}_2\text{O} + \text{Li}_2\text{O} = \text{Li}_2\text{O}_2\text{H}_2$ ,  $\Delta_r H^\circ(0) = -84.1 \text{ kcal mol}^{-1}$  ( $-351.9 \text{ kJ mol}^{-1}$ );

$2\text{LiOH} = \text{Li}_2\text{O}_2\text{H}_2$ ,  $\Delta_r H^\circ(0) = -63.2 \text{ kcal mol}^{-1}$  ( $-264.4 \text{ kJ mol}^{-1}$ );

Zero-point correction was applied in [82RAG] using vibrational frequencies calculated with 3-21G basis set. Using enthalpy of formation values for  $\text{H}_2\text{O}(\text{g})$  and  $\text{Li}_2\text{O}$  from [82GUR/VEI] in combination with the values adopted for  $\text{LiOH}(\text{g})$  (see Section 2.2.1) results in the following values  $\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0)$ :  $-757.3$  and  $-718.6 \text{ kJ mol}^{-1}$ , respectively.

[83SOL/POG]

Solomonik and Pogrebnaya carried out *ab initio* study of  $\text{LiOH}$  and  $\text{Li}_2\text{O}_2\text{H}_2$  molecules using Husinagi-Dunning double-zeta basis set DZHD and modified DZHD basis sets with different functions on the O atom. From the total energy values for  $\text{LiOH}$  and  $\text{Li}_2\text{O}_2\text{H}_2$ , Solomonik and Pogrebnaya obtained the enthalpy of  $\text{LiOH}$  dimerization:



Zero-point correction was calculated using vibration frequencies of  $\text{LiOH}$  and  $\text{Li}_2\text{O}_2\text{H}_2$  molecules obtained in the same work. The values obtained show very weak dependence on the basis set. The mean value  $\Delta_r H^\circ(0) = -268.6 \text{ kJ mol}^{-1}$  corresponds to the enthalpy of formation  $\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0) = -722.8 \text{ kJ mol}^{-1}$ .

[84HOD/SOL]

Hodošček and Šolmajer performed the energy decomposition analysis for dimerization of lithium first-row hydrides. They obtained the value  $-88.3 \text{ kcal mol}^{-1}$  ( $-369.4 \text{ kJ mol}^{-1}$ ) for  $\text{LiOH}$  dimerization energy using *ab initio* SCF



method with 4-31G basis set. This value corresponds to the enthalpy of formation  $\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0) = -823.6 \text{ kJ mol}^{-1}$ .

[84KAU/KLA]

Kaufmann *et al.* carried out *ab initio* calculations of LiOH dimerization energy at various theoretical levels. The final value  $\Delta_f H^\circ(0) = -68.9 \text{ kcal mol}^{-1}$  ( $-288.3 \text{ kJ mol}^{-1}$ ) was obtained with 6-31G\* basis set. Electron correlation was estimated using Møller–Plesset perturbation theory to second order. This value corresponds to the enthalpy of formation  $\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0) = -742.5 \text{ kJ mol}^{-1}$ .

#### Discussion of the Enthalpy of Formation Data

The authors of this review have recalculated equilibrium constant values from the experimental works annotated above with the thermal functions from this work and auxiliary data from [82GUR/VEY] and [89GUR/VEY]. The recalculated values of enthalpies of reaction and the values of enthalpy of formation of  $\text{Li}_2\text{O}_2\text{H}_2(\text{g})$  are given in Table 2-24; results of quantum-mechanical calculations are collected in Table 2-25. In the case of experimental determinations the results of the second and third-law treatment are presented; error assessments represent statistical uncertainty (95% confidence level). For the enthalpy of formation, the values derived from the third-law treatment are given. Error assessments represent a total uncertainty estimate, obtained on the basis of all error constituents (statistical uncertainty, estimate of systematic error in equilibrium constant values, uncertainty of thermal functions and auxiliary thermochemical data).

Berkowitz *et al.* [60BER/MES] studied three equilibria involving the formation of  $\text{Li}_2\text{O}_2\text{H}_2(\text{g})$ : reactions (3), (4) and (5). For the reaction (5), only two measurements of ion currents were carried out, and the partial pressure of  $\text{Li}_2\text{O}_2\text{D}_2$  was very low. For this reason, reaction (5) cannot be re-

garded as a source of reliable information on  $\text{Li}_2\text{O}_2\text{H}_2$  stability. In the case of reaction (4) it is necessary to recalculate the equilibrium constant values for the same reasons as in the case of  $\text{LiOH}(\text{g})$ . There is no need to recalculate reaction (3) because of reactions (2), (3) and (4) only two are independent; reaction (2) was recalculated earlier. The equilibrium constant of reaction (4) can be represented in the form  $K^\circ = (P(\text{LiOH})/P(\text{Li}_2\text{O}_2\text{H}_2)) \cdot P(\text{LiOH})$ . The ratio  $P(\text{LiOH})/P(\text{Li}_2\text{O}_2\text{H}_2)$  can be retained unchanged, because, as it follows from the comparison of data in the Table I and Table IV in [60BER/MES], the ionization cross section ratio of monomer and dimer is near to 1:1.2, in agreement with the experimental ratio for lithium halides. The value  $P(\text{LiOH})$  was corrected by multiplying by 0.3, following from the previous analysis for  $\text{LiOH}(\text{g})$ . After correcting all equilibrium constant values for reaction (4) the following third-law enthalpy value was obtained:  $\Delta_f H^\circ(0) = 271.9 \text{ kJ mol}^{-1}$ . The enthalpy of formation corresponding to this value is

$$\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0) = -726.2 \text{ kJ mol}^{-1}.$$

Results obtained by Berkowitz Mattuck and Buechler [63BER/BUE] cannot be regarded as reliable, because the experimental data apparently do not correspond to equilibrium conditions, and kinetic analysis of the data is not free from some arbitrary assumptions. Possibly the authors [63BER/BUE] overestimated in their analysis the degree of undersaturation and underestimated the importance of diffusion. The results of theoretical calculations (except [84HOD/SOL]) are in reasonable agreement with the value, recalculated from the work of Berkowitz *et al.* [60BER/MES].

The value adopted in this review is based on the work [60BER/MES] (as corrected):

$$\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 298.15 \text{ K}) = -737 \pm 10 \text{ kJ mol}^{-1}.$$

Comparison with the values recommended in selected reference books is given in Table 2-26.

2.2.4. Appendix. Tables of Experimental and Evaluated Data for  $\text{Li}_2\text{O}_2\text{H}_2(\text{g})$ TABLE 2-23. Equilibrium constant values for reaction  $\text{Li}_2\text{O}_2\text{H}_2(\text{g}) = 2\text{LiOH}(\text{g})$ , [60BER/MES].

N	T/K	P/mm Hg	$(K^\circ)^{-1}$
1	1350	0.16( $\text{H}_2\text{O}$ )	108.2
2	1306	0.16( $\text{H}_2\text{O}$ )	255
3	1270	0.16( $\text{H}_2\text{O}$ )	467
4	1226	0.16( $\text{H}_2\text{O}$ )	1432
5	1152	0.16( $\text{H}_2\text{O}$ )	6610
6	1119	0.04( $\text{H}_2\text{O}$ )	11530
7	1241	0.04( $\text{H}_2\text{O}$ )	695
8	1314	0.04( $\text{H}_2\text{O}$ )	316
9	1182	0.04( $\text{H}_2\text{O}$ )	1863
10	1352	0.04( $\text{H}_2\text{O}$ )	248
11	1154	0.05( $\text{D}_2\text{O}$ )	3200
12	1221	0.05( $\text{D}_2\text{O}$ )	827
13	1274	0.05( $\text{D}_2\text{O}$ )	328
14	1310	0.05( $\text{D}_2\text{O}$ )	140
15	1357	0.05( $\text{D}_2\text{O}$ )	71.7
16	1403	0.05( $\text{D}_2\text{O}$ )	32.5
17	1448	0.05( $\text{D}_2\text{O}$ )	22.4
18	1394	0.022	60.5
19	1410	0.110	38.2

TABLE 2-24. Results of experimental determinations of  $\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0)$ ,  $\text{kJ mol}^{-1}$ .

Reference	Method	$\Delta_f H^\circ(0)$		
		Second law	Third law	$\Delta_f H^\circ(0)$ Third law
[60BER/MES]	Knudsen effusion mass spectrometry, $\text{Li}_2\text{O}_2\text{H}_2(\text{g}) = 2\text{LiOH}(\text{g})$ , 1119–1410 K (19 points)	$247.8 \pm 20$	$271.9 \pm 1.4$	$-713.2 \pm 8$
	$2\text{LiOD}(\text{cr}) = \text{Li}_2\text{O}_2\text{D}_2(\text{g})$ , 559.5 K and 598.0 K (2 points)	...	$201.6 \pm 6$	$-762.0 \pm 10$
[63BER/BUE]	Transpiration, $\text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g}) = \text{Li}_2\text{O}_2\text{H}_2(\text{g})$ , 1095 and 1145 K (2 points)	...	$61.6 \pm 5$	$-768.8 \pm 50$

<sup>a</sup>Recalculated values (see the text).TABLE 2-25. Results of quantum-mechanical calculations of  $\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0)$ .

Reference	$\Delta_f H^\circ(\text{Li}_2\text{O}_2\text{H}_2, \text{g}, 0)$ $\text{kJ mol}^{-1}$
[82RAG]	$-718.6^a$
	$-757.3^b$
[83SOL/POG]	$-722.8$
[84HOD/SOL]	$-823.6$
[84KAU/CLA]	$-742.5$

<sup>a</sup>Reaction:  $\text{H}_2\text{O} + \text{Li}_2\text{O} = \text{Li}_2\text{O}_2\text{H}_2$ .<sup>b</sup>Reaction:  $2\text{LiOH} = \text{Li}_2\text{O}_2\text{H}_2$ .TABLE 2-26. Comparison of the heat capacity, enthalpy, entropy, and enthalpy of formation values for  $\text{Li}_2\text{O}_2\text{H}_2(\text{g})$ .

Reference	$C_p^\circ(298.15 \text{ K})$	$S^\circ(298.15)$	$H^\circ(298.15 \text{ K})$	$\Delta_f H^\circ$
	$\text{J K}^{-1} \text{ mol}^{-1}$		$-H^\circ(0)$	(298.15 K)
			$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$
82MED/BER	91.6	282.8	17.85	$-719.8 \pm 21$
82GUR/VEY	91.580	282.979	17.853	$-723.6 \pm 20$
85CHA/DAV	71.223	269.794	14.502	$-711.3 \pm 33.5$
Adopted	79.886	270.723	15.578	$-737 \pm 10$

TABLE 2-27. Thermodynamic functions at 0.1 MPa:  $\text{Li}_2\text{O}_2\text{H}_2(\text{g})$ .

T(K)	$C_p^\circ$	$-(G^\circ - H^\circ(0))T^{-1}$	$S^\circ$	$H^\circ - H^\circ(0)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
	J (mol K) <sup>-1</sup>			kJ mol <sup>-1</sup>		
0	0.000	0.000	0.000	0.000	-726.166	-726.166
25	33.258	126.830	160.058	0.831	-726.595	-725.880
50	33.628	149.873	183.161	1.664	-727.432	-724.886
75	35.959	163.433	197.159	2.529	-728.499	-723.384
100	40.151	173.266	208.045	3.478	-729.576	-721.512
150	50.808	187.983	226.285	5.745	-731.702	-717.015
200	61.914	199.608	242.435	8.565	-733.782	-711.749
250	71.897	209.683	257.352	11.917	-735.539	-706.032
300	80.160	218.798	271.218	15.726	-737.052	-699.997
350	86.737	227.217	284.089	19.905	-738.331	-693.718
400	91.898	235.081	296.022	24.376	-739.483	-687.264
450	95.951	242.475	307.090	29.077	-740.618	-680.668
500	99.159	249.457	317.371	33.957	-741.760	-673.333
600	103.836	262.354	335.892	44.123	-749.644	-658.262
700	107.076	274.045	352.156	54.677	-751.165	-642.908
800	109.520	284.30	366.620	65.512	-752.445	-627.354
900	111.515	294.564	379.638	76.566	-753.559	-611.649
1000	113.239	303.672	391.478	87.806	-754.552	-595.826
1100	114.781	312.155	402.344	99.208	-755.456	-579.911
1200	116.185	320.095	412.393	110.758	-756.295	-563.914
1300	117.471	327.558	421.744	122.441	-757.095	-547.848
1400	118.651	334.602	430.493	134.248	-757.872	-531.726
1500	119.733	341.271	438.717	146.168	-758.646	-515.545
1600	120.724	347.607	446.476	158.192	-759.437	-499.312
1700	121.629	353.640	453.823	170.310	-1049.958	-469.007
1800	122.456	359.402	460.799	182.515	-1048.965	-434.864
1900	123.210	364.914	467.440	194.799	-1047.961	-400.772
2000	123.897	370.200	473.778	207.155	-1046.950	-366.740
2200	125.096	380.164	485.644	232.058	-1044.925	-298.817
2400	126.094	389.415	496.573	257.180	-1042.941	-231.072
2600	126.930	398.052	506.700	282.484	-1041.041	-163.494
2800	127.634	406.153	516.133	307.943	-1039.269	-96.063
3000	128.229	413.783	524.960	333.531	-1037.655	-28.750
3200	128.736	420.993	533.252	359.229	-1036.236	38.466
3400	129.169	427.829	541.070	385.020	-1035.045	105.598
3600	129.543	434.327	548.464	410.892	-1034.105	172.668
3800	129.867	440.520	555.477	436.834	-1033.431	239.689
4000	130.149	446.436	562.146	462.836	-1033.037	306.687
4200	130.396	452.099	568.502	488.891	-1032.935	373.663
4400	130.614	457.529	574.573	514.993	-1033.124	440.645
4600	130.806	462.745	580.383	541.135	-1033.611	507.649
4800	130.977	467.763	585.954	567.313	-1034.372	574.682
5000	131.128	472.599	591.304	593.525	-1035.412	641.734
5200	131.265	477.264	596.449	619.764	-1036.705	708.850
5400	131.387	481.771	601.406	646.030	-1038.247	776.009
5600	131.497	486.129	606.186	672.318	-1040.002	843.234
5800	131.597	490.349	610.802	698.627	-1041.956	910.528
6000	131.687	494.439	615.265	724.956	-1044.074	977.898
298.150	79.886	218.474	270.723	15.578	-737.000	-700.225
Uncertainties in Functions						
0	0.000	0.000	0.000	0.000	8.000	8.000
298.15	2.000	1.000	2.000	0.300	8.000	8.000
1000	3.000	2.500	4.000	1.500	9.000	8.000
2000	3.500	4.000	6.000	4.000	9.000	10.000
3000	4.000	6.000	8.000	6.000	10.000	17.000
4000	5.000	8.000	10.000	8.000	12.000	30.000
5000	6.000	10.000	12.000	10.000	13.000	50.000
6000	7.000	12.000	14.000	12.000	15.000	70.000

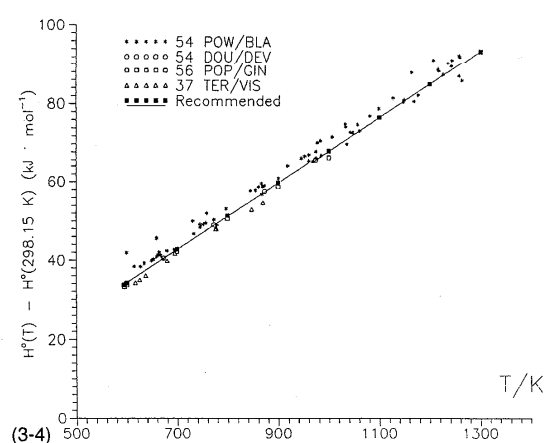
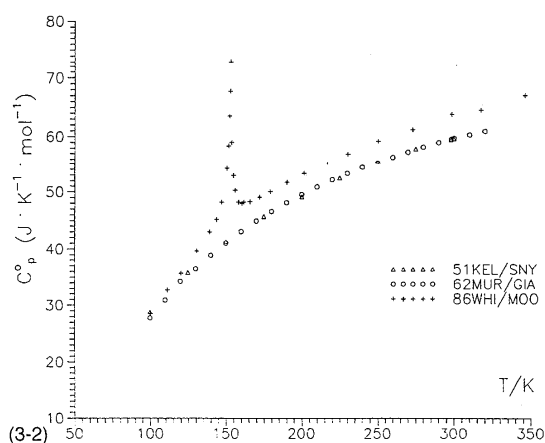
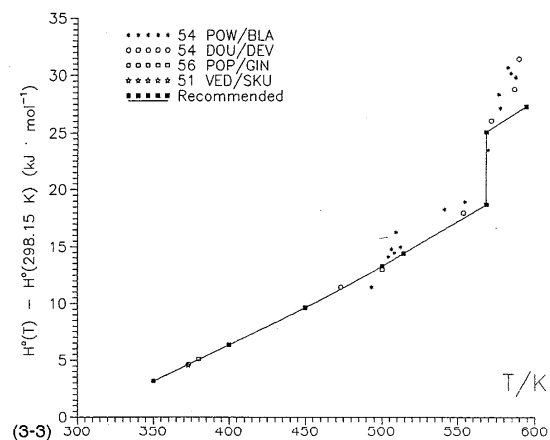
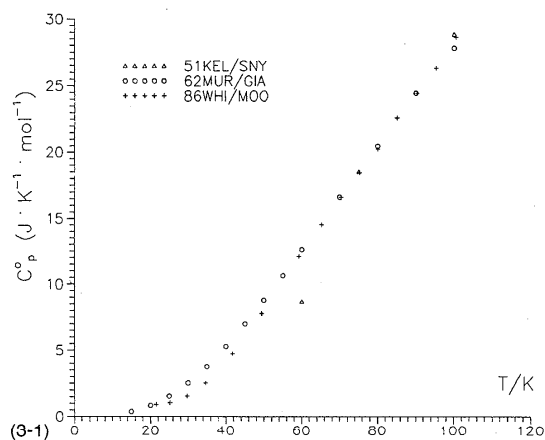


FIG. (3-1). Heat capacity of NaOH and NaOD (86WHI/MOO) at 10–100 K.

(3-2) Heat capacity of NaOH and NaOD (86WHI/MOO) at 100–320 K.

(3-3) Enthalpy  $H^\circ(T) - H^\circ(298.15 \text{ K})$  for solid NaOH at 298.15–594 K.

(3-4) Enthalpy  $H^\circ(T) - H^\circ(298.15 \text{ K})$  for liquid NaOH at 594–1300 K.

### 3. Sodium Hydroxide

#### 3.1. Sodium Hydroxide in Condensed Phases

##### 3.1.1. Heat Capacity and Enthalpy Measurements

###### Temperatures below 298.15 K

[51KEL/SNY], [51KEL/SNY2]

Kelly and Snyder measured the heat capacity of NaOH in an adiabatic calorimeter at 60–300 K. The commercial sample of NaOH, containing about 1.1%  $\text{H}_2\text{O}$  and 1.2%  $\text{Na}_2\text{CO}_3$ , was dissolved in the absolute ethanol. The sodium monoalcoholate obtained was purified and then decomposed to NaOH by heating for 30 hours. Analysis showed that the resulting sample contained no less than 99.84% NaOH and no more than 0.02%  $\text{Na}_2\text{CO}_3$ , 0.02%  $\text{SiO}_2$  and 0.005%  $\text{Cl}^-$ . 22.36 g of NaOH was used for the measurements. The low temperature adiabatic calorimeter was described in the paper [33SOU/BRI]. A resistance thermometer, made from alloy Pt-10%Rh and calibrated according to recommendations of IPTS-48, was used for temperature measurements.

The authors [51KEL/SNY] reported only smoothed heat capacity values at 60 K and in the range 75–300 K every 25 K. Extrapolation of the heat capacity below 60 K by a combination of Debye and Einstein functions led to  $S^\circ(60 \text{ K}) = 4.85 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $H^\circ(60 \text{ K}) - H^\circ(0) = 216 \text{ J mol}^{-1}$ . The results of this study are listed in Table 3-1 and shown in Figs. 3-1 and 3-2.

[62MUR/GIA]

Murch and Giauque measured the heat capacity of NaOH (58 data points) in the temperature range 12.7–315.9 K. The sample was prepared by the reaction of sodium metal (containing less than 0.01 mol % of impurities) with water and consequent drying of the sample by heating at about 350 °C for 10 hours. According to the chemical analysis, the final NaOH sample contained about 4 mol % of  $\text{H}_2\text{O}$  and 0.01 mol % of  $\text{Na}_2\text{CO}_3$ ; it has the formula  $\text{NaOH} \cdot 0.04014 \text{ H}_2\text{O}$ . In this study the authors also measured the heat capacity of  $\text{NaOH} \cdot \text{H}_2\text{O}$ . Corrections for the  $\text{NaOH} \cdot \text{H}_2\text{O}$  could be made in the calculation of the heat capacity of pure NaOH. The measurements were carried out on the adiabatic calorimeter

made from gold; its construction was very similar to that described in [37GIA/EGA]. The temperature was measured by platinum resistance thermometer calibrated by the US NBS. The authors [62MUR/GIA] did not estimate an accuracy, but it apparently was within the limits 0.3–0.5%, excluding data at lowest temperatures. According to [62MUR/GIA] extrapolation of the heat capacity values below 15 K gave  $S^\circ(15\text{ K})=0.084\text{ J K}^{-1}\text{ mol}^{-1}$  though the use of cubic Debye law gave  $S^\circ(15\text{ K})=1/3 C_p^\circ(15\text{ K})=0.123\text{ J K}^{-1}\text{ mol}^{-1}$ . Taking into account the  $\text{H}_2\text{O}$  contamination of the sample (as  $\text{NaOH}\cdot\text{H}_2\text{O}$ ), the authors [62MUR/GIA] prepared the table of smoothed heat capacity values for pure NaOH in the range from 15 to 320 K. Using additional high temperature data [54DOU/DEV], the authors [62MUR/GIA] calculated thermal functions of solid NaOH (15–592.3 K) and liquid NaOH (592.3–1000 K). The results of this study are listed in Table 3-2 and shown in Figs. 3-1 and 3-2. These data are evidently the most accurate at the present time.

#### [86WHI/MOO]

White and Moore measured the heat capacity of NaOD at temperatures from 21.56 K to 346.09 K (Table 3-2). The sample of NaOD was prepared by dehydration of NaOD solution in  $\text{D}_2\text{O}$  carried out in a zirconium crucible under vacuum at 160 °C. The sample contained the following impurities:  $\text{D}_2\text{O}$  (<0.2 mass %),  $^1\text{H}$  ( $4\pm 2$  mol %) and  $\text{Na}_2\text{CO}_3$  (2.5 mass %, as determined by x-ray powder diffraction). The heat capacity of 15.768 g of powdered NaOD was measured in a heat-pulse adiabatic calorimeter with a known accuracy of  $\pm 1\%$ ; 137 experimental values were obtained (see Figs. 3-1 and 3-2). The authors [86WHI/MOO] observed  $\lambda$ -anomaly in the heat capacity curve between 140–170 K centered at  $153.2\pm 0.1$  K. The enthalpy of the transition was derived from integration of the excess heat capacity from just below the transition to just above it; the results are  $\Delta_{\text{tr}}H=131.1\pm 0.7\text{ J mol}^{-1}$  and  $\Delta_{\text{tr}}S=0.864\pm 0.005\text{ J K}^{-1}\text{ mol}^{-1}$ . Various studies such as dielectric measurements, x-ray analysis [86BAS/ELC2], NMR and DTA studies [85AMM/BAS] show that this low temperature transition clearly occurs in NaOD but not in NaOH, at least under the atmospheric pressure and at the temperatures greater than 6 K. However this transition may represent a high pressure modification of sodium hydroxide (NaOH IV) detected in [69PIS] under the pressure 9 kbar. This supposition is based on the fact that substitution of a hydrogen with a heavier isotope is equivalent to application of high pressure [80HUE].

#### Temperatures above 298.15 K

##### [37TER/VIS]

Terashkevich and Vishnevskii measured the enthalpy of NaOH(liq).  $H(T)-H(295.15\text{ K})$ , in the temperature range 617–870 K. The water drop calorimeter was used. The container for the NaOH sample was made from phosphorus-molybdenum steel; its volume was about  $6\text{ cm}^3$ . Information concerning interaction of liquid NaOH with the container was not presented in the paper. Five NaOH samples containing 2.0–19.7%  $\text{Na}_2\text{CO}_3$  were investigated. The sample con-

taining minimal  $\text{Na}_2\text{CO}_3$  impurity (up to 2%) represented the commercial (“Kahlbaum”) NaOH that was dehydrated by metallic Na and then heated at 400–450 °C. The accuracy of the enthalpy measurements was estimated as  $\sim 2\%$  (maximal uncertainty). From the results of 9 measurements (see Table 3-3) the authors [37TER/VIS] derived the heat capacity of NaOH(liq) in the range 633–823 K as  $0.483\text{ cal K}^{-1}\text{ g}^{-1}=80.8\text{ J K}^{-1}\text{ mol}^{-1}$ . This value is about 5% lower than the value adopted in this review. The accuracy of these data is rather low.

##### [51VED/SKU]

Vedenev and Skuratov measured the value of enthalpy of NaOH between 19 and 100 °C. A commercial sample of NaOH (“Kahlbaum”) containing about 6%  $\text{H}_2\text{O}$  was dehydrated in a dry stream of  $\text{N}_2$  by heating in a silver container at 420 °C, then in vacuum ( $p=3\text{ mm Hg}$ ) during twenty-four hours. According to the chemical analysis the sample contained 2.13%  $\text{Na}_2\text{CO}_3$ , 0.4%  $\text{H}_2\text{O}$  and 97.17% NaOH. The measurements of enthalpy were made in a massive copper drop-calorimeter calibrated by measurements of the heat capacity of water. Six measurements were made; the average value of the “mean heat capacity” was calculated as  $C_p(19\text{--}100\text{ }^\circ\text{C})=0.3754\pm 0.0012\text{ cal K}^{-1}\text{ g}^{-1}$ . After including the corrections on  $\text{Na}_2\text{CO}_3$  and  $\text{H}_2\text{O}$  impurities the values  $0.3780\text{ cal K}^{-1}\text{ g}^{-1}=15.12\text{ cal K}^{-1}\text{ mol}^{-1}$  or  $H(373.15\text{ K})-H(292.15\text{ K})=5124\text{ J mol}^{-1}$  and  $H(373.15\text{ K})-H(298.15\text{ K})=4586\text{ J mol}^{-1}$  were obtained. The last value is 1.3% lower than the corresponding value obtained by [54DOU/DEV] (Table 3-4).

##### [54DOU/DEV]

Douglas and Dever measured the enthalpy of NaOH by drop calorimetry from 373 to 974 K. The samples were obtained from the Oak Ridge National Laboratory, which gave as its analysis “100.0 percent ( $\pm 0.05\%$ ) alkalinity, calculated as NaOH; 0.05%  $\text{Na}_2\text{CO}_3$ .” Analysis of these samples made by [54DOU/DEV] gave a different result: NaOH—99.2–99.4%,  $\text{Na}_2\text{CO}_3$ —0.27–0.33%,  $\text{H}_2\text{O}$ —0.4%. The measurements of enthalpy were made in a Bunsen ice calorimeter described in [54DOU/DEV2]. Oxygen-free silver was selected as the container material. The measurements for  $T < 973\text{ K}$  showed no signs of reaction between NaOH and the container material. But after heating up to 1073 K the container became very brittle and showed signs of deterioration. Thirty-six measurements of enthalpy for three NaOH samples in three different containers at 11 temperatures were made. The enthalpies of the empty containers, accounting for 50–60% of enthalpy of the system container+NaOH sample, were determined by a separate series of measurements at the same temperatures. Only two measurements of the enthalpy of NaOH in two different containers were made at the highest temperature 701.2 °C. In total 13 experimental values of enthalpy were obtained: 4 values for  $\alpha$ -NaOH, 3 values for  $\beta$ -NaOH and 6 values for liquid NaOH (see Table 3-5 and Figs. 3-3 and 3-4). Corrections for contaminations were made only for  $\beta$ -NaOH (571–589 K) as these results were greatly distorted by premelting phenomenon. The influence

of these corrections on the value of enthalpy of transition (at 292.8 °C) and fusion (at 319.1 °C) is evident. On the basis of the data obtained the authors [54DOU/DEV] calculated enthalpy values (in J g<sup>-1</sup>):

$$\alpha\text{-NaOH, } 0\text{--}292.8\text{ }^{\circ}\text{C: } H(t) - H(0\text{ }^{\circ}\text{C}) = 1.4764t + 2.195 \cdot 10^{-4} t^2 + 1.968 \times 10^{-6} t^3$$

$$\text{Transition, } 292.8\text{ }^{\circ}\text{C: } \Delta_{\text{trs}}H = 158.9,$$

$$\beta\text{-NaOH, } 292.8\text{--}319.1\text{ }^{\circ}\text{C: } H(t) - H(0\text{ }^{\circ}\text{C}) = 29.9 + 2.15 t,$$

$$\text{Fusion, } 319.1\text{ }^{\circ}\text{C: } \Delta_{\text{fus}}H = 158.9,$$

$$\text{Liquid NaOH, } 319.1\text{--}700\text{ }^{\circ}\text{C: } H(t) - H(0\text{ }^{\circ}\text{C}) = 180.6 + 2.199t - 7.31 \times 10^{-5} t^2.$$

The authors did not estimate the accuracy of their data. The reproducibility of these data are high enough (in the limits 0.1–0.2%), but taking into account the possible systematic errors, associated with the sample impurities, the uncertainties of these data are estimated as 0.5%.

#### [54POW/BLA]

Powers and Blalock measured the enthalpy of solid and liquid NaOH from 493 to 1263 K. According to the chemical analysis, the sample contained 0.13% Na<sub>2</sub>CO<sub>3</sub>. But analysis of the same samples carried out by [54DOU/DEV] showed only 99.2–99.4% NaOH, about 0.3% Na<sub>2</sub>CO<sub>3</sub> and 0.4% H<sub>2</sub>O. Tapered metal capsules made from nickel were used; they were filled with the sample under dry air. Chemical analysis of the sample carried out after measurements showed only a small increase of Na<sub>2</sub>CO<sub>3</sub> impurity (up to 0.28%) and a decrease of total alkalinity from 99.97% to 99.46%. A Bunsen ice calorimeter described previously [51RED/LON] was used. During the experiment, the furnace (in which the capsule was heated before being dropped into the calorimeter) was replaced by a longer one (from 12 inches to 24 inches) allowing for a decrease in the temperature gradient in the furnace and a slight increase in the reproducibility of the results. Only 22 out of 89 measurements were made in the 24 inch-furnace. Reproducibility of the enthalpy measurements of the solid (220–314 °C, 17 experimental points) was poor (about 10–15%) and the authors [54POW/BLA] did not use these results for calculations. From the results of 72 measurements of the enthalpy of liquid NaOH (342–990 °C) the linear equation:  $H(t) - H(0\text{ }^{\circ}\text{C}) = 65.8 + 0.494t$  (in cal g<sup>-1</sup>) and a constant value of heat capacity of liquid NaOH:  $C_p = 0.49 \pm 0.02$  cal K<sup>-1</sup> mol<sup>-1</sup> (82.0 ± 3.4 J K<sup>-1</sup> mol<sup>-1</sup>) were derived. The results of this study are listed in Table 3-4 and shown in Figs. 3-3 and 3-4.

#### [56POP/GIN], [56GIN]

Popov and Ginzburg measured the enthalpy of NaOH by drop calorimetry from 380 to 1016 K. The sample was prepared from a commercial one containing 1% Na<sub>2</sub>CO<sub>3</sub> and 5% H<sub>2</sub>O. Dehydration of the sample was carried out by heating of the melt in vacuum at 400–425 °C during 2 days; according to the chemical analysis data the sample contained 1.2% Na<sub>2</sub>CO<sub>3</sub> and 0.01% other impurities after purification. The capsules from Ni-Cr alloy containing about 80% Ni were used. Absence of the interaction of molten NaOH with the capsule material at high temperatures was confirmed by control measurements of the enthalpy of solid NaOH at

240 °C. The chemical analysis of NaOH samples after the measurements was not carried out. The authors of [56POP/GIN] estimated an uncertainty in their measurements as 0.3%, but actually it is higher, because the Ni-Cr alloy has a polymorphic transition near 300 °C. This transition affects the accuracy of enthalpy measurements of the empty capsules. The authors of [56POP/GIN] carried out 62 measurements of NaOH enthalpy, but the experimental values were not given in the paper.

Statistical treatment of the data [56POP/GIN] was carried out by Ginzburg [56GIN]. The following equations and values were obtained:

Equation for  $\alpha$ -NaOH heat capacity (298.15–576.8 K, cal K<sup>-1</sup> mol<sup>-1</sup>):

$$C_p = 12.228 + 7.995 \times 10^{-3} T,$$

Enthalpy of transition summed with the value  $H(595.16\text{ K}) - H(576.8\text{ K})$ :

$$\Delta_{\text{trs}}H = 1929.7\text{ cal mol}^{-1}.$$

Enthalpy of fusion:  $\Delta_{\text{fus}}H = 1629.3\text{ cal mol}^{-1}$

Equation for heat capacity of liquid NaOH (595.16–1016 K):

$$C_p = 23.997 - 5.4644 \times 10^{-3} T.$$

According to the last equation the heat capacity of liquid NaOH decreases in the range 600–1000 K from 86.7 to 77.54 J K<sup>-1</sup> mol<sup>-1</sup>. The results of this study are listed in Table 3-6 and shown in Figs. 3-3 and 3-4.

#### [87TAK/KAM]

Takahashi *et al.* measured the heat capacity of NaOH from 335 K to 560 K by differential scanning calorimetry (DSC-method). The sample contained 2.5 wt % Na<sub>2</sub>CO<sub>3</sub> and 95.6 wt % NaOH. A container was made of polytetrafluoroethylene. Because of the crystalline transitions at about 290 and 300 K and a fusion at 600 K of polytetrafluoroethylene at about 290, 300 and 600 K the measurements of heat capacity were limited to the interval between 323 and 573 K. The uncertainties of the heat capacity values were reported to be about 2%. The data for the range 330–505 K were tabulated and fitted by the linear equation:

$$C_p^{\circ} = (1.0279 + 1.443 \times 10^{-3} T)\text{ J K}^{-1}\text{ g}^{-1}$$

$$= (41.113 + 57.716 \times 10^{-3} T)\text{ J K}^{-1}\text{ mol}^{-1}.$$

The data above 505 K were presented only in the form of a small graph. At about 518–520 K a sharp change of heat capacity probably connected with phase  $\alpha$ - $\beta$  transition was observed. The heat capacity of  $\beta$ -NaOH at the range from 520 to 560 K was a constant value equal to 2.0 J K<sup>-1</sup> g<sup>-1</sup> = 80 J K<sup>-1</sup> mol<sup>-1</sup>. Above 560 K the  $\beta$ - $\gamma$  transformation of NaOH began.

#### Discussion of Heat Capacity and Enthalpy Data

Figures 3-1 and 3-2 show the low temperature heat capacity values of NaOH [51KEL/SNY] (60–300 K); [62MUR/GIA] (12–316 K) and the analogous values of NaOD

[86WHI/MOO] (22–346 K). Apparently the most pure NaOH samples (containing 99.84% NaOH) have been investigated in [51KEL/SNY]. Unfortunately, the experimental heat capacity values, as well as the data concerning the calorimeter calibration and the accuracy of measurements, are not given in this paper. At 150–300 K the smoothed data of [51KEL/SNY] are in a very good agreement (0.5%) with those of [62MUR/GIA]. At 90–140 K the values from [51KEL/SNY] seem to be overestimated (the maximal deviation from the values presented in [62MUR/GIA] is 5% at 110–130 K). At lower temperatures the heat capacity curves from these two works cross each other (at 75 K) and then the curve [51KEL/SNY] goes down sharply; at 60 K it is 30% lower than the curve of [62MUR/GIA]. Though the NaOH sample from [62MUR/GIA] contained 4 mol % H<sub>2</sub>O, these data should be preferred as the corrections based on the heat capacity values of NaOH·H<sub>2</sub>O were made by the authors. The authors of [62MUR/GIA] carried out the measurements down to 12.7 K; the extrapolation of heat capacity to  $T=0$  resulted in  $S^\circ(15\text{ K})=0.084\text{ J K}^{-1}\text{ mol}^{-1}$ . Note that the values from [62MUR/GIA] are about 20% higher than those from [86WHI/MOO] for NaOD in the range 30–50 K, but at  $T>100\text{ K}$  the heat capacity curve of NaOD lies higher than that of NaOH [62MUR/GIA], the difference being about 6% in the temperature range 200–300 K. The values from [62MUR/GIA] at 30–50 K are probably overestimated. But below 25 K the heat capacity curves from [62MUR/GIA] and [86WHI/MOO] approach each other.

The heat capacity values and other thermodynamic functions calculated in [62MUR/GIA] are listed in Table 3-7. At standard temperature the following values are adopted:

$$\begin{aligned} C_p^\circ(298.15\text{ K}) &= 59.53 \pm 0.3\text{ J K}^{-1}\text{ mol}^{-1}, \\ S^\circ(298.15\text{ K}) &= 64.43 \pm 0.8\text{ J K}^{-1}\text{ mol}^{-1}, \\ H^\circ(298.15\text{ K}) - H^\circ(0) &= 10490 \pm 50\text{ J mol}^{-1}. \end{aligned}$$

These values are compared with those recommended in different reviews in Table 3-8. The uncertainties of the adopted values for  $S^\circ(298.15\text{ K})$  and  $H^\circ(298.15\text{ K}) - H^\circ(0)$  are due to mentioned putative inaccuracy of the data [62MUR/GIA] at the temperatures below 60 K. New measurements of the heat capacity of pure NaOH samples at low temperatures are desirable, especially at  $T < 60\text{ K}$ .

Figure 3-3 shows the enthalpy  $H^\circ(T) - H^\circ(298.15\text{ K})$  of solid NaOH measured in [54DOU/DEV], [56POP/GIN], [51VED/SKU], and [54POW/BLA]. The values  $H^\circ(T) - H^\circ(298.15\text{ K})$  at 350 (50) 500 K calculated by integration of the heat capacities measured in [87TAK/KAM] are also given. The data of all studies of  $\alpha$ -NaOH and  $\beta$ -NaOH (except [54POW/BLA]) agree satisfactorily within 1%. The exception is the temperature range above 500 K, where the divergence between the data of [54DOU/DEV] and [56POP/GIN, 87TAK/KAM] increases to 2%. The equation for heat capacity of the orthorhombic  $\alpha$ -modification of NaOH:

$$\begin{aligned} C_p^\circ/\text{J K}^{-1}\text{ mol}^{-1} &= -797.602 + 5146.32 \cdot 10^{-3} T \\ &+ 87.154 \cdot 10^5 T^{-2} - 11367.7 \times 10^{-6} T^2 \\ &+ 8875.35 \times 10^{-9} T^3 \end{aligned}$$

was derived from the data of 5 studies. Data used were 18 points of the enthalpy increments  $H^\circ(T) - H^\circ(298.15\text{ K})$  that were obtained in 5 studies with the following uncertainties (in brackets): 4 points obtained in [54DOU/DEV] from 11 measurements ( $\pm 0.5\%$ ), 5 points at 270, 280, 290, 310, and 320 K obtained by integration of heat capacities measured in [62MUR/GIA] ( $\pm 0.5\%$ ), 1 point at 373.15 K obtained as the average value of 6 measurements in [51VED/SKU] ( $\pm 1\%$ ), 4 points at 380, 400, 450, and 500 K obtained in [56POP/GIN] ( $\pm 1\%$ ), and 4 points at 350, 400, 450, and 500 K obtained by integration of heat capacities data [87TAK/KAM] ( $\pm 2\%$ ). The enthalpy values of [54POW/BLA] for NaOH(cr) have a large scatter (up to 15%) and therefore they have not been taken into account.

The heat capacities of  $\beta$ -NaOH and  $\gamma$ -NaOH, stable in relatively narrow temperature ranges 514–568 K and 568–594 K, respectively, are adopted as the constant values, because only isolated enthalpy values were obtained in these ranges. For the monoclinic  $\beta$ -modification,  $C_p^\circ=80\text{ J K}^{-1}\text{ mol}^{-1}$  is adopted based on the measurements shown on the graph in study [87TAK/KAM] (it is practically a constant value in the range 520–560 K). These authors estimated uncertainties of their measurements as 2%; in this limit the values [87TAK/KAM] for  $\alpha$ -NaOH are in a good agreement with the other data. For the cubic  $\gamma$ -modification,  $C_p^\circ=86\text{ J K}^{-1}\text{ mol}^{-1}$  as recommended in [54DOU/DEV] is adopted here. It was derived from enthalpy measurements at three temperatures (571, 586, and 589 K) taking into account corrections on Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O impurities.

The adopted values for the heat capacity of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -modifications of NaOH have to be in agreement with recommended values of transitions and fusion enthalpy of NaOH. They should be based on the integral value—the enthalpy increment  $H^\circ(594\text{ K, liq}) - H^\circ(298.15\text{ K, } \alpha)$  for which the value 33660 J mol<sup>-1</sup> was adopted according to the most reliable data of [54DOU/DEV] (see below).

Figure 3-4 shows the enthalpy  $H^\circ(T) - H^\circ(298.15\text{ K})$  of liquid NaOH measured in [54DOU/DEV], [56POP/GIN], [37TER/VIS], and [54POW/BLA]. The data [37TER/VIS] obtained for the NaOH sample containing 2% Na<sub>2</sub>CO<sub>3</sub> lie lower than all the other data, with their deviation from the most reliable values [54DOU/DEV] increasing at higher temperatures (to 4.5% at 870 K). The values from [56POP/GIN] lie a little lower than those from [54DOU/DEV], in the limits 1.5–2%. The highest temperature enthalpy data of liquid NaOH [54POW/BLA] were measured over the temperature range 615–1263 K (72 measurements), but in the range 615–1000 K the reproducibility of these measurements is very poor (the deviations are about 3–4%). The smoothed values of [54POW/BLA] lie 7% higher than those from [54DOU/DEV] at 600 K, 3.5% higher at 800 K and about 2% at 1000 K. In the temperature range 1000–1267 K the smoothed enthalpy values [54POW/BLA] lie only 1.5% higher than the adopted ones.

The most precise measurements of enthalpy of liquid NaOH were made by Douglas and Dever [54DOU/DEV] and these data can be considered as the best at the present time.

The authors [54DOU/DEV] fitted their values from  $T_{\text{fus}}$  to 1000 K to the linear heat capacity:

$$C_p^{\circ}/\text{J K}^{-1} \text{mol}^{-1} = 89.613 - 5.913 \times 10^{-3} T.$$

According to this equation, the heat capacity decreases from  $C_p^{\circ}(594 \text{ K}) = 86.1$  to  $C_p^{\circ}(1000 \text{ K}) = 83.7 \text{ J K}^{-1} \text{mol}^{-1}$ . Above 1000 K the heat capacity of liquid NaOH was adopted as a constant value  $83.7 \text{ J K}^{-1} \text{mol}^{-1}$ .

#### Phase Equilibrium Data

At atmospheric pressure NaOH has three crystal phases (see Table 1-1):  $\alpha$ -NaOH—orthorhombic modification (space group Cmc21 [85JAC/KOC]),  $\beta$ -NaOH—orthorhombic modification (space group P2<sub>1</sub>/m [67STE]) and  $\gamma$ -NaOH—cubic modification (space group Fm3m [73PAP/BOU]). The existence of two additional phases at high pressure was established in the study [69PIS].

A transition ( $\alpha$ - $\beta$ ) at 245 °C had been unknown before the study [71DIO/RES] because of a very small value of heat of transition. This transition was not noticed either in measurements of the enthalpy or by thermal analysis. The works published before 1971 implied the polymorphic transition at  $\approx 300 \text{ C}$  as the transition from rhombic to monoclinic modification of NaOH. It was marked as  $\alpha$ - $\beta$  transition.

Numerous works are devoted to the determination of transition and fusion temperatures of NaOH; phase diagrams of NaOH with other compounds were investigated in many of them. Information concerning the accuracy of the measurements was often absent in these studies. Several works containing evidently erroneous data have not been taken into account. But some information from these works is presented in Tables 3-9 and 3-10.

#### [10HEV2]

Hevesy determined the temperatures and enthalpies of the polymorphic transition and fusion of NaOH by the thermal analysis method. A commercial sample of NaOH ("Kahlbaum") containing about 3% H<sub>2</sub>O was dehydrated in the silver container at 450 °C. The temperature was determined by Ag-Ni thermocouple that was calibrated against the melting point of NaNO<sub>3</sub> (306.1 °C). The cooling curve made with the rate 12 °C/min have shown the following values:  $T_{\text{trs}} = 299.6 \pm 0.5 \text{ }^{\circ}\text{C} = 572.75 \text{ K}$  and  $T_{\text{fus}} = 318.4 \pm 0.2 \text{ }^{\circ}\text{C} = 591.55 \text{ K}$ . The enthalpies of transition and fusion of NaOH were determined by a quantitative DTA method comparing with the standards—NaNO<sub>3</sub> and KNO<sub>3</sub> that have a known enthalpy of fusion. The following values were determined:  $\Delta_{\text{trs}}H = 990 \text{ cal mol}^{-1}$  and  $\Delta_{\text{fus}}H = 1602 \text{ cal mol}^{-1}$ .

#### [15SCA2]

Scarpa studied the system NaOH-NaCl and determined  $T_{\text{trs}} = 303 \pm 2 \text{ }^{\circ}\text{C} = 576 \text{ K}$  and  $T_{\text{fus}} = 310 \text{ }^{\circ}\text{C} = 583 \text{ K}$  by DTA-method. The sample of NaOH contained 2.5% impurities (mostly Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O).

#### [20JAN]

Janecke studied the system NaOH-NaNO<sub>3</sub> and determined  $T_{\text{trs}} = 296 \text{ }^{\circ}\text{C} = 569 \text{ K}$  and  $T_{\text{fus}} = 321 \text{ }^{\circ}\text{C} = 594 \text{ K}$  by thermal analysis.

#### [23EWL]

Ewles obtained a value for the transition temperature of NaOH as 293 °C = 566 K by the disappearance of fluorescence.

#### [26ANT/SOM]

Antropoff and Sommer studied the system NaOH-NaCl and determined  $T_{\text{trs}} = 303 \text{ }^{\circ}\text{C} = 576 \text{ K}$  and  $T_{\text{fus}} = 322 \pm 2 \text{ }^{\circ}\text{C} = 595 \text{ K}$  by thermal analysis. The sample was purified by melting of NaOH in a silver container at 500 °C in a stream of dry N<sub>2</sub>.

#### [34HAL/TOM]

Halla and Tompa obtained the values of  $T_{\text{trs}} = 295.3 \pm 1.3 \text{ }^{\circ}\text{C} = 568.45 \text{ K}$  and  $T_{\text{fus}} = 327.6 \pm 0.9 \text{ }^{\circ}\text{C} = 600.75 \text{ K}$  by a thermal analysis method.

#### [42SEW]

Seward studied the system NaOH-Na<sub>2</sub>CO<sub>3</sub> and determined the values of  $T_{\text{trs}} = 294 \text{ }^{\circ}\text{C} = 567 \text{ K}$  and  $T_{\text{fus}} = 320 \pm 1 \text{ }^{\circ}\text{C} = 593 \text{ K}$  by the DTA method. The enthalpy of fusion equal to 1.67 kcal mol<sup>-1</sup> (7.0 kJ mol<sup>-1</sup>) was calculated from the data of the investigated system.

#### [53KHI/KHI]

Khitrov *et al.* obtained the values of  $T_{\text{trs}} = 298 \text{ }^{\circ}\text{C} = 571 \text{ K}$  and  $T_{\text{fus}} = 322 \text{ }^{\circ}\text{C} = 595 \text{ K}$  by the DTA method. The commercial sample of NaOH ("Kahlbaum") was purified by heating in a silver container in a dry CO<sub>2</sub>-free air stream at 500 °C. Analysis of the sample after purification showed only traces of Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O.

#### [54DOU/DEV]

Douglas and Dever determined the transition and fusion temperatures of NaOH by separate experiments. A silver container with NaOH was placed into the furnace. Its temperature was measured by a platinum resistance thermometer. The cooling-curve technique with very low speed was used. For two samples of NaOH (99.3% purity)  $T_{\text{trs}} = 292.8 \text{ }^{\circ}\text{C} = 565.95 \text{ K}$  was determined. The fusion temperature 315.8–317.2 °C was obtained in 5 experiments. Corrections for impurities have led to the following value of fusion temperature of pure NaOH:  $T_{\text{fus}} = 319.1 \text{ }^{\circ}\text{C} = 592.25 \text{ K}$ .

#### [54RAV/ROR]

Ravich *et al.* studied the system NaOH-Na<sub>2</sub>CO<sub>3</sub> and determined  $T_{\text{trs}} = 304 \text{ }^{\circ}\text{C} = 577 \text{ K}$  and  $T_{\text{fus}} = 327 \text{ }^{\circ}\text{C} = 600 \text{ K}$  by thermal analysis. After purification the sample of NaOH contained 0.46% Na<sub>2</sub>CO<sub>3</sub>.

#### [54BER/RES]

Bergman and Reshetnikov prepared NaOH by the reaction of a pure sodium metal with water. The NaOH sample thus obtained was dehydrated by heating in a silver container in the atmosphere of CO<sub>2</sub> and H<sub>2</sub>O free air. The fusion point  $T_{\text{fus}} = 321 \pm 1 \text{ }^{\circ}\text{C} = 594 \text{ K}$  was obtained by visual method of thermal analysis (observation of crystal appearance upon slow decreasing of the melt temperature). The transition point  $T_{\text{trs}} = 299 \text{ }^{\circ}\text{C} = 572 \text{ K}$  was obtained from a bend of the liquidus curve of the system NaOH-NaNO<sub>3</sub>.



[58RES/UNZ]

Reshetnikov and Unzhakov studied the system NaOH-LiOH and determined the values  $T_{\text{trs}}=299\text{--}300\text{ }^{\circ}\text{C}=572\text{--}573\text{ K}$  and  $T_{\text{fus}}=321\text{--}322\text{ }^{\circ}\text{C}=594\text{--}595\text{ K}$  by thermal analysis.

[59RES/UNZ]

Reshetnikov and Unzhakov purified the NaOH samples by heating in a stream of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  free air at  $450\text{--}500\text{ }^{\circ}\text{C}$ . The determinations of fusion and transition temperatures were made in a silver crucible by DTA and visual method of thermal analysis. The values  $T_{\text{fus}}=322\text{ }^{\circ}\text{C}=595\text{ K}$  and  $T_{\text{trs}}=300\text{ }^{\circ}\text{C}=573\text{ K}$  were obtained.

[59ROL/COH]

Rollet *et al.* prepared the sample of NaOH by electrolysis of  $\text{Na}_2\text{CO}_3$  water solution in a stream of hydrogen, then purified it from  $\text{CO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{ClO}_3^-$  ions and dehydrated up to constant fusion temperature. The temperature was measured with a copper-constantan thermocouple with uncertainty  $0.3\text{ }^{\circ}\text{C}$ . The authors of [59ROL/COH] observed the values  $T_{\text{trs}}=299\text{ }^{\circ}\text{C}=572\text{ K}$  and  $T_{\text{fus}}=321\text{ }^{\circ}\text{C}=594\text{ K}$ .

[61COH/MIC]

Cohen-Adad *et al.* studied the system NaOH- $\text{Na}_2\text{CO}_3$  and determined  $T_{\text{trs}}=297\text{ }^{\circ}\text{C}=570\text{ K}$  and  $T_{\text{fus}}=321\text{ }^{\circ}\text{C}=594\text{ K}$ . The sample of NaOH was prepared according to the method described in the previous study [59ROL/COH].

[61RES/ROM]

Reshetnikov and Romanova studied the system NaOH- $\text{KNO}_2$  and obtained the values  $T_{\text{trs}}=299\text{ }^{\circ}\text{C}=572\text{ K}$  and  $T_{\text{fus}}=322\text{ }^{\circ}\text{C}=595\text{ K}$  for pure NaOH.

[63LUX/BRA]

Lux and Brandl determined the values  $T_{\text{trs}}=298\text{ }^{\circ}\text{C}=571\text{ K}$  and  $T_{\text{fus}}=322\text{--}323\text{ }^{\circ}\text{C}=595\text{--}596\text{ K}$ . The authors were the first to observe that at  $298\text{ }^{\circ}\text{C}$  NaOH had a transition from monoclinic to the high temperature cubic modification at  $289\text{ }^{\circ}\text{C}$ .

[64MOR/BUR]

Morey and Burlew used a NaOH sample containing  $0.22\text{ mol } \%$   $\text{Na}_2\text{CO}_3$ . They studied in detail the diagram of state of the system  $\text{Na}_2\text{O-H}_2\text{O-CO}_2$  near the point corresponding to the stoichiometric composition of NaOH. The measurements were carried out in a platinum crucible, the rate of heating and cooling varied from slightly less than  $1^{\circ}/\text{min}$  to  $2^{\circ}/\text{min}$ . The Pt-Pt/Rh thermocouples used were calibrated at the lead melting point ( $327.35\text{ }^{\circ}\text{C}$ ); the precision of measurements of the transition and the fusion temperatures was  $0.2\text{--}0.3\text{ }^{\circ}\text{C}$ .

The authors of [64MOR/BUR] established that the high temperature modification of NaOH had a region of solid solutions from the stoichiometric composition of NaOH ( $77.37\text{ wt } \%$   $\text{Na}_2\text{O}$ ) to that containing  $76.6\text{ wt } \%$   $\text{Na}_2\text{O}$ ; the temperature of transition in this range varied from  $293.1\pm 0.3\text{ }^{\circ}\text{C}=566.25\text{ K}$  to  $287.7\pm 0.3\text{ }^{\circ}\text{C}=560.85\text{ K}$ . Addition of  $\text{Na}_2\text{CO}_3$  up to the composition corresponding to  $4.1\text{ wt } \%$   $\text{CO}_2$  showed that the temperature of transition was not changed and was equal to  $T_{\text{trs}}$  of the sample containing  $0.22$

$\text{wt } \%$   $\text{CO}_2$ . The fusion temperature of the sample containing  $99.78\text{ mol } \%$  NaOH and  $0.22\text{ mol } \%$   $\text{Na}_2\text{CO}_3$  was determined as  $318\text{ }^{\circ}\text{C}$ . Taking into account  $\text{Na}_2\text{CO}_3$  impurity resulted in a correction of about  $1\text{ }^{\circ}\text{C}$ . The authors of [64MOR/BUR] recommended for the pure NaOH the value  $T_{\text{fus}}=319\pm 2\text{ }^{\circ}\text{C}=592\text{ K}$ .

[65COH/RUB], [67RUB]

Cohen-Adad *et al.* studied the system NaOH-NaCl and determined for pure NaOH  $T_{\text{fus}}=320\text{ }^{\circ}\text{C}=593\text{ K}$ . Ruby studied the system NaOH-NaF and obtained  $T_{\text{trs}}=297\text{ }^{\circ}\text{C}=570\text{ K}$  and  $T_{\text{fus}}=321\text{ }^{\circ}\text{C}=594\text{ K}$ . The samples of NaOH contained  $0.8\%$  impurities, mostly  $\text{Na}_2\text{CO}_3$ .

[65SMI/STR]

Smirnov and Strel'nikova studied the system NaOH- $\text{Na}_2\text{S}$  and determined  $T_{\text{trs}}=305\text{ }^{\circ}\text{C}=578\text{ K}$  and  $T_{\text{fus}}=330\pm 6\text{ }^{\circ}\text{C}=603\text{ K}$ . The sample of NaOH contained  $3.2\%$   $\text{Na}_2\text{CO}_3$ ; an uncertainty of the temperature measurement by Pt-Pt/Rh thermocouple was  $\pm 6\text{ }^{\circ}\text{C}$ . The data are not accurate.

[66MIT/SHI]

Mitkevich and Shikhov studied the system NaOH-Na by the thermal analysis method and determined  $T_{\text{trs}}=292\text{ }^{\circ}\text{C}=565\text{ K}$  and  $T_{\text{fus}}=320\text{ }^{\circ}\text{C}=593\text{ K}$ .

[67RES/BAR], [69RES/BAR]

Reshetnikov and Baranskaya investigated a sample of NaOH containing about  $0.2\text{--}0.4\%$   $\text{Na}_2\text{CO}_3$  and  $0.1\%$   $\text{H}_2\text{O}$ . The transition temperature was determined as  $299\pm 1\text{ }^{\circ}\text{C}=572\text{ K}$ ; the fusion temperature was determined by DTA method ( $322\pm 1\text{ }^{\circ}\text{C}=595\text{ K}$ ) and by visual method of thermal analysis ( $323\pm 1\text{ }^{\circ}\text{C}=596\text{ K}$ ). The enthalpy of transition ( $1.72\text{ kcal mol}^{-1}=7.2\text{ kJ mol}^{-1}$ ) was determined by quantitative differential thermal analysis with accuracy about  $10\%$ . The enthalpy of fusion of NaOH ( $1.575\text{ kcal mol}^{-1}=6.59\text{ kJ mol}^{-1}$ ) was adopted by [67RES/BAR] as a standard; this value is the mean of two determinations in [54DOU/DEV] ( $6.36\text{ kJ mol}^{-1}$ ) and [56POP/GIN] ( $6.82\text{ kJ mol}^{-1}$ ).

[69PIS]

Pistorius investigated the phase diagram of NaOH at high pressure up to  $40\text{ kilobars}$ . The commercial sample of NaOH ("Merck") contained  $1\%$   $\text{Na}_2\text{CO}_3$  as the main impurity; the data concerning other impurities are not given. The sample was carefully dried before use. The transition temperature at atmospheric pressure was found to be  $291\pm 2\text{ }^{\circ}\text{C}=564\text{ K}$ . It was obtained by DTA method as the mean of twelve determinations. In this study three new phases stable at high pressure were investigated and the coordinates (temperatures and pressures) of 4 triple points were determined. The author of [69PIS] believed that the cubic phase is stable at high pressure only.

[73PAP/BOU]

Papin and Bouaziz studied polymorphism in NaOH. X-ray analysis confirmed the existence of 3 polymorphic modifications at normal pressure: orthorhombic ( $\alpha$ -NaOH), monoclinic ( $\beta$ -NaOH) and cubic ( $\gamma$ -NaOH). The temperatures of the  $\beta$ - $\gamma$  transition and  $\alpha$ - $\beta$  transition were determined by

the DTA method (the curves of heating were analyzed) as 297 °C=570 K and 245 °C=518 K, respectively. The former had enthalpy of transition comparable with the enthalpy of fusion of NaOH; the latter had a very small enthalpy of transition (there was only a bend in the DTA curve).

[80CHR/PAP]

Christmann and Papin studied the system NaOH-LiOH and determined  $T_{\text{trs}}=297\text{ °C}=570\text{ K}$  and  $T_{\text{fus}}=321\text{ °C}=594\text{ K}$  by thermal analysis method.

[82BLE/DAC]

Bleif and Dachs measured the heat capacity of NaOH from 400 K to 600 K. The heat capacity was determined by heating or cooling of the sample in a roughly constant heat flow, and by numerical differentiation of the temperature curve. An accuracy of the energy scale is 20% only, therefore this study has significance only for investigation of the phase transitions, but not for determination of the absolute heat capacity values. The temperature scale was calibrated by the melting points of Sn (505.0 K), Bi (544.2 K) and Pb (600.6 K). The commercial sample of NaOH ("Merck") had a purity of 99%; the main impurities being H<sub>2</sub>O and less than 1% Na<sub>2</sub>CO<sub>3</sub>. Purification of the sample was made by heating in vacuum at 720 K for several hours. The temperature of the  $\alpha$ - $\beta$  transition was obtained as 514 K. The enthalpy of transition proved to be very small and was not determined. The authors of [82BLE/DAC] considered this transition as of the displacement type (a phase transition of the second kind). The temperature of  $\beta$ - $\gamma$  transition was determined to be 566 K and the fusion point as 591 K. Taking into account an influence of Na<sub>2</sub>CO<sub>3</sub> impurity (0.4 wt %), the authors of [82BLE/DAC] adopted the value 592 K for the pure NaOH.

For the NaOD sample the following data were obtained:

$$T_{\text{trs}}(\alpha-\beta)=500\text{ K}, T_{\text{trs}}(\beta-\gamma)=561\text{ K}, \text{ and } T_{\text{fus}}=593\text{ K}.$$

[85CHI/MAR]

Chiotti and Markuszewski studied the systems NaOH-Na<sub>2</sub>O and NaOH-Na<sub>2</sub>CO<sub>3</sub>. Analytical-grade NaOH was dried by heating under vacuum at 300–310 °C for 4 hours. Analysis of the dried product indicated 99.7±0.1 mol % NaOH and 0.3±0.1 mol % Na<sub>2</sub>CO<sub>3</sub>. Temperatures were measured with a chromel-alumel thermocouple calibrated to the melting points of Zn (419.5 °C) and Mg (649 °C). The polymorphic transition point at 291 °C was obtained. [85CHI/MAR] noted that it was lower than other literature data due to small amounts of residual water and Na<sub>2</sub>CO<sub>3</sub> in the sample.

#### Discussion of Phase Equilibrium Data

The polymorphic transition from orthorhombic to the monoclinic modification is a phase transition of displacement type [82BLE/DAC] and is followed by a heat effect so small that it had not been noticed before 1971 either by thermal analysis or by enthalpy measurements. The authors of [56POP/GIN] pointed out that "the mean heat capacity curve turns up at 230 °C (503 K) indicating a beginning of

polymorphic transition," but they have not carried out the detailed investigation.

The temperature of the  $\alpha$ - $\beta$  transition in the range from 513 K to 520 K was determined in four studies (see Table 3-9). The value  $T_{\text{trs}}=514\text{ K}$  [82BLE/DAC] should be preferred, it was determined from heat capacity measurements, its uncertainty may be estimated as ±3 °C.

Measurements of the temperature of NaOH  $\beta$ - $\gamma$  transition (see Table 3-9) result in values in the range from 560 to 578 K. According to the detailed investigation [64MOR/BUR] Na<sub>2</sub>CO<sub>3</sub> impurity up to 4 wt % does not influence significantly  $T_{\text{trs}}$  while 1% H<sub>2</sub>O impurity decreases  $T_{\text{trs}}$  by 5.5 K (from 566.45 K to 560.95 K). The low value of  $T_{\text{trs}}=560.45\text{ K}$  given in [54SMO/KRU] is probably explained by H<sub>2</sub>O contamination of the sample.

The comparatively high scatter of the data of other studies (at the range 566–578 K) probably results from errors in the measurements by the thermal analysis method. Because of the high value of the enthalpy of transition, as measured by DTA, the thermal effect on the thermogram is rather broad, especially in the case of quick heating, resulting in the difficulties of determination of the equilibrium transition temperature.

In particular, as concerns the studies reporting the highest values of  $T_{\text{trs}}$  from 576 to 578 K; we do not take these data into account. The next three groups of works we consider to be the more reliable:

- (1) The works [54DOU/DEV], [64MOR/BUR] and [82BLE/DAC] present the value  $T_{\text{trs}}=566\text{ K}$ ; the first two of them indicate that the thermal analysis was carried out with rather low rate of heating.
- (2) The works of French investigators ([59ROL/COH] and others) gave the value  $T_{\text{trs}}=570\text{ K}$ ; this temperature was measured very carefully in these works.
- (3) The works of Reshetnikov and co-authors give the values from 570 to 573 K (570 K from the latest work [71DIO/RES]).

Since the reasons for the discrepancy of all these data cannot be explained at the present time, the average value  $T_{\text{trs}}(\beta-\gamma)=568\pm 2\text{ K}$  is adopted here.

The results of numerous measurements of the NaOH fusion temperature carried out after 1910 (see Table 3-10) are scattered in the range from 583 to 603 K. Relatively old studies give underestimated values of melting point. Several studies are not considered to be accurate because of the use of impure samples or the use of inaccurate methods of  $T_{\text{fus}}$  determination.

The most reliable studies give the fusion temperatures from 592 to 596 K. The adopted fusion temperature  $T_{\text{fus}}=594\pm 2\text{ K}$  is based on the data of French investigators [59ROL/COH, 61COH/MIS, 67RUB, 73PAP/BOU] that give the value  $T_{\text{fus}}=594\text{ K}$ . In study [59ROH/COH] the temperature was measured with an uncertainty 0.3 K. The group of works that gave  $T_{\text{fus}}=592\text{ K}$  investigated the samples of NaOH with impurities of Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O that gave "premelting effect" in heat capacity [54DOU/DEV, 82BLE/

DAC]. The data of [67RES/BAR] gave the rather overestimated value 596 K. New determinations of melting point of pure NaOH are necessary.

The polymorphic transition from orthorhombic ( $\alpha$ ) to monoclinic ( $\beta$ ) modification at 514 K is considered to be of displacement type [82BLE/DAC] and appears to be a phase transition of the second order. Upon the measuring of the heat capacity of NaOH, a  $\lambda$ -transition has been detected [87TAK/KAM], but the data of this study are insufficient to conclude whether there is isothermic heat in this case. We adopt that  $\Delta_{\text{trs}}H(\alpha-\beta)=0$ .

The values of the enthalpy of the  $\beta$ - $\gamma$  transition and the enthalpy of fusion of NaOH have to be selected together with the values of heat capacity of all modifications of solid NaOH considering the value of the enthalpy increment  $H^\circ(594 \text{ K, liq})-H^\circ(298.15 \text{ K, } \alpha)$  as the most reliable. As it was established above, this value is equal to  $33660 \text{ J mol}^{-1}$  according to the most precise data of [54DOU/DEV]. The summation adopted here for the enthalpy increments for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -modification of NaOH and the values of enthalpy of  $\beta$ - $\gamma$  transition ( $6360 \text{ J mol}^{-1}$ ) and fusion (the same value  $6360 \text{ J mol}^{-1}$ ) obtained by [54DOU/DEV] results in the value  $33674 \text{ J mol}^{-1}$ . It agrees with the experimental value almost completely. Thus, we adopt here the values obtained by [54DOU/DEV] with the following uncertainties:  $\Delta_{\text{trs}}H(\beta-\gamma)=6360\pm 300 \text{ J mol}^{-1}$  and  $\Delta_{\text{fus}}H=6360\pm 400 \text{ J mol}^{-1}$ . The data of the other authors appear to be less reliable (see Tables 3-11 and 3-12).

#### Calculation of Thermal Functions of NaOH(cr and l)

The thermal functions of NaOH(cr) for the temperatures 15–298.15 K (Table 3-7) are listed from the data [62MUR/GIA]. The following values are adopted:

$$\begin{aligned} C_p^\circ(298.15 \text{ K}) &= 59.53 \pm 0.3 \text{ J K}^{-1} \text{ mol}^{-1}, \\ S^\circ(298.15 \text{ K}) &= 64.43 \pm 0.8 \text{ J K}^{-1} \text{ mol}^{-1}, \\ H^\circ(298.15 \text{ K}) - H^\circ(0) &= 10490 \pm 50 \text{ J mol}^{-1}. \end{aligned}$$

The thermal functions of NaOH (cr and liq) for the temperatures 0–2000 K (Table 3-15) are calculated using the adopted values and equations presented in the previous section and data of Table 3-7.

#### Heat Capacity Equations:

$$\begin{aligned} \alpha\text{-NaOH (298.15–514 K):} \\ C_p^\circ/\text{J K}^{-1} \text{ mol}^{-1} &= -797.602 + 5146.320 \times 10^{-3} T \\ &+ 87.154 \times 10^5 T^{-2} - 11367.7 \times 10^{-6} T^2 + 8875.35 \times 10^{-9} T^3, \\ \beta\text{-NaOH (514–568 K): } C_p^\circ/\text{J K}^{-1} \text{ mol}^{-1} &= 80, \\ \gamma\text{-NaOH (568–594 K): } C_p^\circ/\text{J K}^{-1} \text{ mol}^{-1} &= 86, \\ \text{Liquid NaOH: (594–1000 K): } C_p^\circ/\text{J K}^{-1} \text{ mol}^{-1} &= 89.613 \\ &- 5.913 \times 10^{-3} T, \\ \text{Liquid NaOH: (1000–2000 K): } C_p^\circ/\text{J K}^{-1} \text{ mol}^{-1} &= 83.7. \end{aligned}$$

#### Phase Equilibrium Data:

$$\begin{aligned} \text{Temperature of } \alpha\text{-}\beta \text{ transition: } T_{\text{trs}}/\text{K} &= 514 \pm 3, \\ \text{Enthalpy of } \alpha\text{-}\beta \text{ transition: } \Delta_{\text{trs}}H/\text{J mol}^{-1} &= 0, \\ \text{Temperature of } \beta\text{-}\gamma \text{ transition: } T_{\text{trs}}/\text{K} &= 568 \pm 2, \\ \text{Enthalpy of } \beta\text{-}\gamma \text{ transition: } \Delta_{\text{trs}}H/\text{J mol}^{-1} &= 6360 \pm 300, \\ \text{Temperature of fusion: } T_{\text{fus}}/\text{K} &= 594 \pm 2, \end{aligned}$$

$$\text{Enthalpy of fusion: } \Delta_{\text{fus}}H/\text{J mol}^{-1} = 6360 \pm 400.$$

The uncertainties of the tabulated values at 298.15, 1000, and 2000 K are listed in Table 3-15. The calculated values of thermal functions of NaOH(cr) are close to those listed in the reference books [82GUR/VEY] and [85CHA/DAV]. For liquid NaOH, the differences increase with temperature reaching 2 and 3  $\text{J K}^{-1} \text{ mol}^{-1}$  at 2000 K in  $\Phi^\circ(T)$  and  $S^\circ(T)$ , respectively, (see Table 3-13) due to the use of the different data for the enthalpy of fusion and heat capacity of liquid NaOH in this study.

### 3.1.2. Enthalpy of formation of NaOH(cr)

The enthalpy of formation of crystalline sodium hydroxide can be obtained from its enthalpy of solution in water and appropriate auxiliary data. The enthalpies of solution of NaOH(cr) in water have been determined by the various investigators and these data are summarized in the Table 3-14.

#### Calorimetric Measurements

##### [1875BER3]

The data obtained by Berthelot [1875BER3], Thomsen [1886THO] and Forcrand [01FOR] (measurements with NaOH(cr)) were recalculated by Parker [65PAR] (Table 3-14) taking into account the changes of atomic weights and the corrections for transition to a standard temperature and infinite dilution. Her recommendations are listed in the Table, column 6.

Berthelot measured the enthalpy of solution of NaOH(cr) in water in a calorimeter at 283.6 K. His result is not particularly reliable. Precision of temperature measurements, the NaOH sample purity and the method of analysis of the final solution were not indicated, and could easily have been sources of error (Table 3-15).

##### [1886THO]

The data obtained by Berthelot [1875BER3], Thomsen [1886THO] and Forcrand [01FOR] (measurements with NaOH(cr)) were recalculated by Parker [65PAR] (Table 3-14) taking into account the changes of atomic weights and the corrections for transition to a standard temperature and infinite dilution. Her recommendations are listed in the Table, column 6.

Thomsen measured the enthalpy of solution of NaOH(cr) in water at 290.5 K, using an isoperibol calorimeter. The energy equivalent of the calorimeter was determined by a sum of heat capacities of all substances and parts of it. This method is not sufficiently reliable. No data concerning purity and composition of the initial NaOH sample were given. The Thomsen result is not to be considered as accurate.

##### [01FOR]

The data obtained by Berthelot [1875BER3], Thomsen [1886THO] and Forcrand [01FOR] (measurements with NaOH(cr)) were recalculated by Parker [65PAR] (Table

3-14) taking into account the changes of atomic weights and the corrections for transition to a standard temperature and infinite dilution. Her recommendations are listed in the Table, column 6.

Forcand measured the enthalpies of solution in water of a sample of NaOH(cr) (1 experiment) and a series of solids contained various amounts of water in the range NaOH(0.3–1.15)H<sub>2</sub>O (11 experiments). The isoperibol calorimeter was used. The Forcand data are fitted well by the equation  $\Delta_{\text{aq}}H/\text{kJ mol}^{-1} = -44.2 \pm 21.6n$ , where  $n$ —the number moles of water in NaOH· $n$ H<sub>2</sub>O-sample (our treatment by a least squares method). The  $\Delta_{\text{aq}}H$  value is equal  $-44.2 \text{ kJ mol}^{-1}$  if  $n=0$  (see column 5 in the Table 3-14). Some essential details of measurements were absent (the initial sample purity, a precision of temperature measurements and so on).

[42ROT/WIR]

Roth *et al.* measured the enthalpies of solution of NaOH(cr) in water in a isoperibol calorimeter at 293.15 K. The calorimeter calibration was carried out using an electrical method. No information about analyses of the NaOH sample and final solution was given. Two  $\Delta_{\text{aq}}H^\circ(\text{NaOH,cr} \Rightarrow n\text{H}_2\text{O}, 293.15 \text{ K})$  values were obtained,  $-39.5 \text{ kJ mol}^{-1}$  ( $n=5.5$ ) and  $-42.6 \text{ kJ mol}^{-1}$  ( $n=421$ ). These results yield a mean value of  $\Delta_{\text{aq}}H^\circ(\text{NaOH,cr} \Rightarrow \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -43.4 \pm 2.1 \text{ kJ mol}^{-1}$  (see Table 3-14, column 6).

[50BOB/LAR]

The enthalpy of solution of NaOH(cr) in water was measured at 296.15 K (1 experiment). An electrically heated twin differential calorimeter of a special design was used. The energy equivalent of the calorimeter was found by dissolving potassium chloride in water. The temperature was recorded on a Beckmann thermometer with a precision of  $\pm 0.001 \text{ K}$ . Other information about the experiment details and a purity of the NaOH sample was not given.

[61RES]

Reshetnikov measured the enthalpy of solution of NaOH(cr) in water in a isoperibol calorimeter at 298.15 K. The temperature was recorded on a platinum resistance thermometer with a resolution of  $\pm 0.0005 \text{ K}$ . The energy equivalent of the calorimeter was determined by an electrical method. The calorimeter had been checked by measuring the enthalpy of solution of potassium chloride ( $\Delta_{\text{aq}}H^\circ(298.15 \text{ K}) = 17548 \pm 13 \text{ J mol}^{-1}$ ); this result is in excellent agreement with the best literature data (see [82MED/BER];  $\Delta_{\text{aq}}H^\circ(298.15 \text{ K}) = 17531 \pm 15 \text{ J mol}^{-1}$ ). The author declared that his NaOH sample was pure; however, he did not quantitatively specify the amount of impurities. All preparative handlings as well as the loading of the calorimeter sample holder were made in a nitrogen filled glove box.

[62MUR/GIA]

Murch and Giauque measured the enthalpies of solution in water of a series of solids that contained various amounts of water in the range NaOH.(0.1 to 1)H<sub>2</sub>O. They used a precise isoperibol calorimeter (the resolution of temperature measurements was  $\pm 0.0003 \text{ K}$ ) and five solid samples of various proportions of NaOH and H<sub>2</sub>O. The samples were prepared

by passing moist nitrogen (purified from CO<sub>2</sub>) over sodium metal (a purity  $>99.99 \text{ mol } \%$ ), followed by drying. The compositions were NaOH.0.11810H<sub>2</sub>O, NaOH.0.26192H<sub>2</sub>O, NaOH.0.51715H<sub>2</sub>O, NaOH.0.79230H<sub>2</sub>O and NaOH.0.97447H<sub>2</sub>O. The analysis method consisted in titrating aliquot parts of samples by a standard sulfuric acid; the amount of water in the samples was obtained by difference. The quantity of Na<sub>2</sub>CO<sub>3</sub> impurity in the samples was very small ( $<0.01 \text{ mol } \%$ ). All final solutions had a composition corresponding NaOH.180H<sub>2</sub>O. The calorimetric results recalculated to infinite dilution have indicated a linear relationship between the enthalpy of solution and the ratio of the moles of water to the moles of NaOH. The value  $\Delta_{\text{aq}}H^\circ(\text{NaOH,cr} \Rightarrow \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -44.57 \pm 0.04 \text{ kJ mol}^{-1}$  was obtained by extrapolation of these data to zero moles of water. It seems that the given error of this value is too small. The Murch and Giauque data can be fitted by the equation  $\Delta_{\text{aq}}H^\circ/\text{kJ mol}^{-1} = -43.92 + 23.093n$ , where  $n$ —number of moles of water in initial NaOH· $n$ H<sub>2</sub>O-samples (our calculation, by the least squares method). The  $\Delta_{\text{aq}}H^\circ$ -value is equal  $-43.92 \text{ kJ mol}^{-1}$  (column 5 in Table 3-14), when  $n=0$ . The average deviation of the experimental  $\Delta_{\text{aq}}H^\circ$ -values from those calculated from the equation indicated above is  $\pm 0.15 \text{ kJ mol}^{-1}$ . The uncertainty of the  $\Delta_{\text{aq}}H^\circ$ -value at  $n=0$  was evaluated as equal approximately  $\pm 0.2 \text{ kJ mol}^{-1}$ .

[72HAR/MOO]

Hartshorn *et al.* measured the enthalpy of solution of NaOH(cr) in water in an isoperibol calorimeter at 298.15 K. The initial sodium hydroxide sample contained 96–97% NaOH and was used without any additional purification. The amount of NaOH in the sample was determined by titration against standard HCl(aq) after carrying out the calorimetric measurements. Two values of the  $\Delta_{\text{aq}}H^\circ(298.15 \text{ K})$  were obtained for the reaction  $\text{NaOH}(\text{cr}) + n\text{H}_2\text{O}(\text{liq}) = \text{NaOH}(\text{soln}, n\text{H}_2\text{O})$ ; they are equal  $-42.19 \text{ kJ mol}^{-1}$  ( $n=3327$ ) and  $-43.95 \text{ kJ mol}^{-1}$  ( $n=3704$ ). Some other details of the experiment (composition of impurities in the NaOH sample, the precision of temperature measurements and so on) were missing.

[73FUC/HAG]

Fuchs and Hagan measured the enthalpy of solution of NaOH(cr) in water in an isoperibol calorimeter at 298.15 K. The molar concentrations of final solutions were  $5 \cdot 10^{-4} - 1 \cdot 10^{-3} \text{ mol l}^{-1}$ . The temperature of the calorimeter was measured by thermistor with a resolution of  $\pm 0.001 \text{ K}$ . The NaOH sample had a stated purity of 99%. Other information about the sample was absent. The mean value of  $\Delta_{\text{aq}}H^\circ(298.15 \text{ K})$  was obtained for the reaction  $\text{NaOH}(\text{cr}) + n\text{H}_2\text{O}(\text{liq}) = \text{NaOH}(\text{soln}, n\text{H}_2\text{O})$ . It was equal to  $-43.9_3 \pm 1.0 \text{ kJ mol}^{-1}$  (the number of measurements was not indicated, but it was more than three). Some other details of measurements were missing; a table of original data was not given. It was essential that final NaOH solutions were dilute,

and therefore corrections for transition to infinite dilution were very small.

#### Discussion of the Enthalpy of Formation Data

The results of the first studies ([1875BER3], [1886THO], [01FOR]) have only historical interest because at that time experimental techniques, methods and materials were of poor quality. From the results of other works, listed in Table 3-14, the data by Murch and Giauque [62MUR/GIA] seem to be the most accurate. These authors used a precise isoperibol calorimeter and five carefully characterized samples of NaOH with compositions from NaOH.0.11810H<sub>2</sub>O to NaOH.0.97447H<sub>2</sub>O. These data indicated a linear dependence of enthalpy of solution from ratio of the moles of water per moles of sodium hydroxide in the initial sample. The  $\Delta_{\text{aq}}H^\circ(\text{NaOH,cr} \rightarrow \infty\text{H}_2\text{O}, 298.15 \text{ K})$  value (see Table 3-14) was obtained by extrapolation of these data to zero moles of water. The uncertainty of value was evaluated in the course of the present work as equal  $\pm 0.2 \text{ kJ mol}^{-1}$  due to the inaccuracies of the samples analyses and extrapolation. The method of determination of the enthalpy of formation of NaOH(cr) used in the work [62MUR/GIA] seems to be more accurate than the measurement of the enthalpy of solution of arid NaOH(cr).

Other results are less reliable. The data of many authors ([42ROT/WIR], [50BOB/LAR], [72HAR/MOO]) can be considered as approximate because they did not set as a goal determining a precise value of  $\Delta_{\text{aq}}H^\circ(\text{NaOH,cr} \rightarrow n\text{H}_2\text{O})$ . Their samples had a worse quality than used by Murch and Giauque, and some important details of their measurements (see abstracts of their papers) were missing. The results of Reshetnikov [61RES] and Fuchs and Hagan [73FUC/HAG] seem to be some more precise, but their NaOH samples were not specified in sufficient details.

The adopted value of enthalpy of formation of crystalline sodium hydroxide is based on the result of Murch and Giauque as the most reliable (see Table 3-14):

$$\Delta_f H^\circ(\text{NaOH,cr}, 298.15 \text{ K}) = -425.8 \pm 0.2 \text{ kJ mol}^{-1}.$$

It is in good agreement with the values of  $\Delta_f H^\circ(\text{NaOH,cr}, 298.15 \text{ K})$  based on the measurements by Reshetnikov [61RES] and Fuchs and Hagan [73FUC/HAG] (see Table 3-14).

The adopted value of  $\Delta_f H^\circ(\text{NaOH,cr}, 298.15 \text{ K})$  and the values, recommended in other critical reviews, are compared in Table 3-8.

#### 3.1.3. Appendix. Tables of Experimental and Evaluated Data for NaOH(cr)

TABLE 3-1. Smoothed heat capacity values of NaOH [51KEL/SNY].

T K	$C_p$	
	cal K <sup>-1</sup> mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>
60	2.075	8.68
75	4.417	18.48
100	6.877	28.77
125	8.553	35.79
150	9.870	41.30
175	10.92	45.69
200	11.76	49.20
225	12.54	52.47
250	13.25	55.44
275	13.83	57.86
298.15	14.21	59.45
300	14.24	59.58

TABLE 3-2. Smoothed heat capacity values of NaOH [62MUR/GIA].

T K	$C_p$	
	cal K <sup>-1</sup> mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>
15	0.088	0.368
20	0.198	0.828
25	0.364	1.523
30	0.597	2.498
35	0.895	3.745
40	1.263	5.284
45	1.671	6.991
50	2.098	8.778
55	2.545	10.65
60	3.016	12.62
70	3.967	16.60
80	4.877	20.41
90	5.832	24.40
100	6.631	27.74
110	7.384	30.89
120	8.185	34.25
130	8.717	36.47
140	9.292	38.88
150	9.810	41.05
160	10.294	43.07
170	10.737	44.92
180	11.140	46.61
190	11.510	48.16
200	11.850	49.58
210	12.172	50.93
220	12.468	52.17
230	12.737	53.29
240	12.996	54.38
250	13.238	55.39
260	13.472	56.37
270	13.694	57.30
280	13.900	58.16
290	14.086	58.94
298.15	14.228	59.53
300	14.260	59.66
310	14.413	60.30
320	14.561	60.92

TABLE 3-3. Experimental enthalpy values  $H^\circ(T) - H^\circ(295.15 \text{ K})$  of NaOH(liq) [37TER/VIS].

N	T K	$H^\circ(T) - H^\circ(295.15 \text{ K})$	
		cal g <sup>-1</sup>	J mol <sup>-1</sup>
1	617(liq)	205.36	34366
2	625	209.76	35103
3	637	216.23	36185
4	680	239.01	39998
5	696	250.66	41947
6	776	287.23	48067
7	778	287.79	48161
8	847	317.30	53099
9	870	327.50	54806

TABLE 3-4. Experimental enthalpy values  $H^\circ(T) - H^\circ(273.15 \text{ K})$  of NaOH [54POW/BLA].

N	T K	$H^\circ(T) - H^\circ(273.15 \text{ K})$	
		cal g <sup>-1</sup>	J mol <sup>-1</sup>
1	493	77	12890
2	504	93	15560
3	506	97	16230
4	508	95	15900
5	509	106	17740
6	512	98	16400
7	513	127	21250
8	541	118	19750
9	554(cr,α)	122	20420
10	566(cr,β)	189	31630
11	569	149	24940
12	576	178	29790
13	577	171	28620
14	582	192	32130
15	584	189	31630
16	587(cr,β)	187	31290
17	599(liq)	259	43340
18	615	238	39830
19	627	238	39830
20	634	243	40670
21	649	247	41340
22	653	249	41670
23	659	253	42340
24	659	281	47030
25	662	256	42840
26	663	256	42840
27	664	260	43510
28	667	255	42670
29	671	250	41840
30	680	262	43850
31	694	264	44180
32	731	307	51380
33	733	288	48200
34	745	302	50540
35	746	298	49870
36	752	302	50540
37	757	304	50870
38	759	319	53380
39	773	309	51710
40	779	301	50370
41	797	326	54560
42	801	316	52880
43	845	353	59070
44	855	354	59240
45	861	359	60080
46	867	364	60920
47	868	348	58240
48	869	365	61080
49	873	361	60410
50	901	372	62250
51	919	391	65430
52	946	405	67780
53	953	408	68280
54	961	401	67110
55	961	410	68610
56	969	400	66940
57	970	400	66940
58	975	405	67780
59	975	415	69450
60	977	428	71630
61	983	431	72130
62	985	409	68450

TABLE 3-4. Continued.

N	T K	$H^\circ(T) - H^\circ(273.15 \text{ K})$	
		cal g <sup>-1</sup>	J mol <sup>-1</sup>
63	1007	437	73130
64	1033	456	76310
65	1034	452	75640
66	1036	426	71290
67	1043	444	74300
68	1048	443	74140
69	1057	455	76140
70	1061	446	74640
71	1081	468	78320
72	1099	479	80160
73	1127	513	85850
74	1148	489	81830
75	1149	492	82340
76	1164	533	89200
77	1169	490	82000
78	1177	499	83510
79	1207	553	92540
80	1216	538	90030
81	1217	535	89530
82	1226	530	88700
83	1235	548	91710
84	1242	543	90870
85	1243	553	92540
86	1257	528	88360
87	1257	560	93720
88	1259	558	93380
89	1263	521	87190

TABLE 3-5. Experimental enthalpy values  $H^\circ(T) - H^\circ(273.15 \text{ K})$  of NaOH [54DOU/DEV].

N	T K	$H^\circ(T) - H^\circ(273.15 \text{ K})$	
		J g <sup>-1</sup>	J mol <sup>-1</sup>
1	373.15	152.8	6112
2	473.15	322.4	12895
3	553.15	486.5	19459
4	553.15(cr,α)	486.0	19439
5	571.15(cr,β)	687.7	27506
6	586.15	756.6	30262
7	589.15(cr,β)	822.5	32898
8	598.15(liq)	886.9	35473
9	673.15	1049.8	41989
10	773.15	1260.8	50428
11	873.15	1473.9	58952
12	974.35	1686.3	67447
13	974.35	1686.8	67467

TABLE 3-6. Smoothed heat capacity and enthalpy values of NaOH [56POP/GIN], [56GIN].

T(K)	$C_p^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>	$H^\circ(T) - H^\circ(298.15 \text{ K})$ J mol <sup>-1</sup>
500	67.89	13020
576.8(cr,α)	70.46	18330
595.16(cr,β)	...	26405
595.16(liq)	86.80	33220
600	86.69	33640
700	84.40	42190
800	82.11	50520
900	79.83	58610
1000	77.54	66480

TABLE 3-7. Thermal functions of NaOH(cr) below 298.15 K.

T K	$C_p^\circ(T)$ J K <sup>-1</sup> mol <sup>-1</sup>	$H^\circ(T) - H^\circ(0)$ J mol <sup>-1</sup>	$S^\circ(T)$ J K <sup>-1</sup> mol <sup>-1</sup>
15	0.368	0.816	0.0837
20	0.828	3.68	0.247
25	1.523	9.41	0.498
30	2.498	19.3	0.858
35	3.745	34.9	1.335
40	5.284	57.4	1.933
45	6.991	87.9	2.653
50	8.778	127	3.481
60	12.62	234	5.414
70	16.60	380	7.657
80	20.41	566	10.134
90	24.40	792	12.786
100	27.74	1052	15.530
120	34.25	1669	21.142
140	38.88	2398	26.748
160	43.07	3219	32.221
180	46.61	4117	37.505
200	49.58	5081	42.576
220	52.17	6098	47.426
240	54.38	7164	52.062
260	56.37	8272	56.497
280	58.16	9418	60.739
298.15	59.53	10490	64.430

TABLE 3-8. Comparison of the heat capacity, enthalpy, entropy and enthalpy of formation values for NaOH(cr).

Reference	$C_p^\circ(298.15 \text{ K})$ J K <sup>-1</sup> mol <sup>-1</sup>	$S^\circ(298.15 \text{ K})$ J K <sup>-1</sup> mol <sup>-1</sup>	$H^\circ(298.15 \text{ K}) - H^\circ(0)$ J mol <sup>-1</sup>	$\Delta_f H^\circ(298.15 \text{ K})$ kJ mol <sup>-1</sup>
82MED/BER	59.54 ± 0.13	64.43 ± 0.20	10485 ± 40	-425.93 ± 0.25
82WAG/EVA	59.54	64.455	10489	-425.609
82GUR/VEY	59.54	64.43 ± 0.20	10490 ± 40	-425.88 ± 0.15
85CHA/DAV	59.53	64.445 ± 0.84	10487	-425.93 ± 0.4
89KON/COR	...	...	...	-425.85 ± 0.08
Adopted	59.53 ± 0.3	64.43 ± 0.8	10490 ± 50	-425.8 ± 0.2

TABLE 3-9. Temperatures of phase transformations of NaOH.

Reference	$T_{tr}/^{\circ}\text{C}$	$T_{tr}/\text{K}$	Comments
Original Studies			
10HEV	299.6±0.5	572.75	Thermal analysis
15SCA2	303±2	576	Thermal analysis (DTA)
20JAN	296	569	Thermal analysis
23EWL	293	566	Fluorescence method
26ANT/SOM	303	576	Thermal analysis
34HAL/TOM	295.3±1.3	568.45	Thermal analysis
42SEW	294	567	Thermal analysis (DTA)
53KHI/KHI	298	571	Thermal analysis (DTA)
54BER/RES	299	572	Thermal analysis
54DOU/DEV	292.8	565.95	Thermal analysis
54RAV/BOR	304	577	Thermal analysis
54SMO/KRU	287.3	560.45	Thermal analysis (DTA)
58RFS/VII	299	572	Thermal analysis
59RES/UNZ	300	573	Thermal analysis
59ROL/COH	297	570	Thermal analysis (DTA)
61COH/MIC	297	570	Thermal analysis
61RES/ROM	299	572	Thermal analysis
63LUX/BRA	298	571	Thermal analysis
64MOR/BUR	293.1±0.3	566.25	Thermal analysis
65SMI/STR	305	578	Thermal analysis
66MIT/SHI	292	565	Thermal analysis
67RES/BAR	299±1	572	Thermal analysis
69PIS	291±2	564	Thermal analysis (DTA)
71DIO/RES	245	518( $\alpha$ - $\beta$ )	Thermal analysis
	297	570( $\beta$ - $\gamma$ )	Thermal analysis
73OVE/SHE	300±3	573	Thermal analysis
73PAP/BOU	245	518	( $\alpha$ - $\beta$ ) Thermal analysis
	297	570( $\beta$ - $\gamma$ )	( $\alpha$ - $\beta$ ) Thermal analysis
80CHR/PAP	297	570	Thermal analysis
82BLE/DAC	241	514( $\alpha$ - $\beta$ )	Heat capacity measur.
	293	566( $\beta$ - $\gamma$ )	Heat capacity measur.
85CHI/MAR	291.1	564.25	Thermal analysis (DTA)
87TAK/KAM	245-247	518-520	( $\alpha$ - $\beta$ ) Heat capacity measur.
Reviews			
82GUR/VEY		572±3	Based on 67RES/BAR
85CHA/DAV		572	Based on 67RES/BAR
Adopted			
This study		514±3( $\alpha$ - $\beta$ ) 568±2( $\beta$ - $\gamma$ )	Based on 82BLE/DAC

TABLE 3-10. Temperature of fusion of NaOH.

Reference	$T_{fus}/^{\circ}\text{C}$	$T_{fus}/\text{K}$	Comments
Original Studies			
10HEV	318.4±0.2	591.55	Thermal analysis
15SCA2	310	583	Thermal analysis
	(DTA)		
20JAN	321	594	Thermal analysis
26ANT/SOM	322±2	595	Thermal analysis
34HAL/TOM	327.6±0.9	600.75	Thermal analysis
42SEW	320±1	593	Thermal analysis (DTA)
53KHI/KHI	322	595	Thermal analysis (DTA)
54BER/RES	321	594	Thermal analysis, visual method
54DOU/DEV	319.1	592.25	Thermal analysis
54RAV/BOR	327	600	Thermal analysis
58RES/UNZ	321-322	594-595	Thermal analysis
59RES/UNZ	322	595	Thermal analysis, visual method
58ROL/COH	321	594	Thermal analysis (DTA)
61COH/MIC	321	594	Thermal analysis
61RES/ROM	322	595	Thermal analysis
63LUX/BRA	322-323	595-596	Thermal analysis
64MOR/BUR	319±2	592	Thermal analysis
65COH/RUB	320	593	Thermal analysis
65SMI/STR	330±6	603	Thermal analysis
66MIT/SHI	320	593	Thermal analysis
67RES/BAR	323	596	Thermal analysis
67RUB	321	594	Thermal analysis
73OVE/SHE	324±3	597	Thermal analysis
73PAP/BOU	321	594	Thermal analysis
80CHR/PAP	321	594	Thermal analysis
82BLE/DOC	319	592	Thermal analysis
Reviews			
82GUR/VEY		596±2	Based on 67RES/BAR
85CHA/DAV		596	Based on 67RES/BAR
Adopted			
This study		594±2	

TABLE 3-11. Enthalpy of  $\beta$ - $\gamma$  transition of NaOH.

Reference	$\Delta_{tr}H$	$\Delta_{tr}H/\text{J mol}^{-1}$	Comments
Original Studies			
10HEV	990 cal mol <sup>-1</sup>	4140	Thermal analysis (DTA)
54DOU/DEV	158.9 J g <sup>-1</sup>	6360	Enthalpy measurements
56POP/GIN		6500	Enthalpy measurements
67RES/BAR	1720 cal mol <sup>-1</sup>	7200	Thermal analysis (DTA)
Reviews			
82GUR/VEY		5850±600	Based on 54DOU/DEV
85CHA/DAV		7196±840	Based on 54DOU/DEV, 56POP/GIN, 67RES/BAR
Adopted			
This study		6360±300	Based on 54DOU/DEV



TABLE 3-12. Enthalpy of fusion of NaOH.

Reference	$\Delta_{\text{fus}}H/J \text{ mol}^{-1}$	Comments
Original Studies		
10HEV	6700	Thermal analysis (DTA)
42SEV	7000	Calculation from the data of the system NaOH-Na <sub>2</sub> CO <sub>3</sub>
54DOU/DEV	6360	Enthalpy measurements
56POP/GIN	6820	Enthalpy measurements
61KRO/STR	8370	Thermal analysis
67RES/BAR	6590	Based on 54DOU/DEV, 56POP/GIN
Reviews		
82GUR/VEY	7800±1500	
85CHA/DAV	6611±840	Based on 54DOU/DEV, 56POP/GIN, 67RES/BAR
Adopted		
This study	6360±400	Based on 54DOU/DEV

TABLE 3-13. Differences (in J K<sup>-1</sup> mol<sup>-1</sup>) between the thermal functions of NaOH(cr and liq) calculated in the present work and in [82GUR/VEY] and in [85CHA/DAV].

T K	[82GUR/VEY]			[85CHA/DAV] <sup>a</sup>		
	$\Delta C_p(T)$	$\Delta\Phi(T)$	$\Delta S(T)$	$\Delta C_p(T)$	$\Delta\Phi(T)$	$\Delta S(T)$
298.15	-0.01	0	0	0	-0.025	-0.015
1000	-0.871	-1.013	-2.530	-0.022	-0.715	-1.778
2000	-1.246	-1.933	-3.154	+5.501	-0.946	-0.072

<sup>a</sup>The values of  $\Phi(T)$  tabulated in [85CHA/DAV] are adjusted to the reference temperature  $T=0$  instead of 298.15 K.

TABLE 3-14. The enthalpy of formation of NaOH (cr) from measurements of the enthalpies of solution of sodium hydroxide in water.

Authors	Moles of H <sub>2</sub> O n <sup>a</sup>	T/K	No. of measurements	$\Delta_{\text{aq}}H^\circ(\text{NaOH},$ $\text{cr} \Rightarrow n\text{H}_2\text{O},$ 298.15 K), <sup>a</sup> kJ·mol <sup>-1</sup>	$\Delta_{\text{aq}}H^\circ(\text{NaOH},$ $\text{cr} \Rightarrow \infty\text{H}_2\text{O},$ 298.15 K), <sup>b</sup> kJ·mol <sup>-1</sup>	$\Delta_f H^\circ(\text{NaOH}, \text{cr},$ 298.15 K), <sup>c</sup> kJ·mol <sup>-1</sup>
[1875BER]	154	283.6	2	-40.9	-43.3±2.1	-427.1±2.1
[1886THO]	163-190	290.5	4	-41.59	-43.12	-427.2
[01FOR]	160	294.6	1	-43.12	-44.10	-426.3
	160	294.6	11	-44.2 <sup>d</sup>	-45.2±0.7	-425.2
[42ROT/WIR]	5.5 and 421	293.15	2	-39.5 and -42.6	-43.4±2.1	-427.0±2.1
[50BOB/LAR]	222	296.15	1	-41.84	-42.64	-427.7
[61RES]	400	298.15	5	-43.70±0.06	-44.16±0.3 <sup>e</sup>	-426.2±0.3
[62MUR/GIA]	180	298.15	5	-43.9 <sup>d</sup>	-44.5±0.2 (the original value is -44.57±0.04)	-425.8±0.2
[72HAR/MOO]	3500	298.15	2	-43.1	-43.1±1.5	-427.1±1.5
[73FUC/HAG]	55555-111111	298.15	more than 3	...	-43.9 <sub>3</sub> ±1.0	-426.4±1.0

<sup>a</sup>Reaction is NaOH(cr)+nH<sub>2</sub>O(liq)=NaOH (soln, nH<sub>2</sub>O).

<sup>b</sup>Reaction is NaOH(cr)+∞H<sub>2</sub>O(liq)=Na<sup>+</sup>(soln, ∞H<sub>2</sub>O)+OH<sup>-</sup>(soln, ∞H<sub>2</sub>O); the calculations were carried out by us with the exception of the Berthelot, Thomsen and Forcrand results (see abstracts of works). The enthalpies of dilution of NaOH(soln, nH<sub>2</sub>O) to infinite dilution for these studies were taken from Parker's book [65PAR].

<sup>c</sup>The CODATA values ( $\Delta_f H^\circ(\text{OH}^-, \text{soln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -230.015 \pm 0.040 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{Na}^+, \text{soln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -240.34 \pm 0.06 \text{ kJ mol}^{-1}$ ) [89COX/WAG] were used in treatment of experimental data. The uncertainty was calculated as a square root from the sum of squares of the uncertainties of  $\Delta_{\text{aq}}H^\circ(298.15 \text{ K})$ ,  $\Delta_f H^\circ(\text{OH}^-, \text{soln}, \infty\text{H}_2\text{O}, 298.15 \text{ K})$  and  $\Delta_f H^\circ(\text{Na}^+, \text{soln}, \infty\text{H}_2\text{O}, 298.15 \text{ K})$ .

<sup>d</sup>The value was obtained by extrapolating of the experimental data for the enthalpies of solution of the NaOH samples containing different amounts of water (from NaOH.0.3H<sub>2</sub>O to NaOH.1.15H<sub>2</sub>O [01FOR] and from NaOH.0.12H<sub>2</sub>O to NaOH.0.97H<sub>2</sub>O [62MUR/GIA]) to zero moles of H<sub>2</sub>O.

<sup>e</sup>The uncertainty was increased to ± 0.3 kJ·mol<sup>-1</sup> owing to the opportunity of presence of some impurities in the NaOH sample.

TABLE 3-15. Thermodynamic functions at 0.1 MPa: NaOH(cr( $\alpha, \beta, \gamma$ ) and liq).

T K	$C_p^\circ$	$-(G^\circ - H^\circ(0))/T$	$S^\circ$	$H^\circ - H^\circ(0)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
	J (mol K) <sup>-1</sup>			kJ mol <sup>-1</sup>		
0	0.000	0.000	0.000	0.000	-421.256	-421.256
25	1.523	0.122	0.498	0.009	-421.918	-419.516
50	8.778	0.941	3.481	0.127	-422.894	-416.787
75	18.490	2.630	8.870	0.468	-423.811	-413.526
100	27.740	5.010	15.530	1.052	-424.501	-409.987
150	41.045	10.853	29.506	2.798	-425.343	-402.525
200	49.580	17.171	42.576	5.081	-425.730	-394.848
250	55.388	23.452	54.304	7.713	-425.852	-387.113
300	59.672	29.464	64.799	10.600	-425.796	-379.365
350	62.743	35.199	74.250	13.668	-425.644	-371.638
400	64.587	40.621	82.751	16.852	-428.102	-363.729
450	68.087	45.739	90.523	20.153	-427.855	-355.696
500	77.912	50.595	98.127	23.766	-427.288	-347.704
514 cr, $\alpha$	82.537	51.920	100.340	24.888	-427.017	-345.479
514 cr, $\beta$	80.000	51.920	100.340	24.888	-427.017	-345.479
550	80.000	55.269	105.755	27.768	-426.325	-339.791
568 cr, $\beta$	80.000	56.910	108.331	29.208	-425.976	-336.965
568 cr, $\gamma$	86.000	56.910	119.529	35.568	-419.616	-336.965
594 cr, $\gamma$	86.000	59.735	123.378	37.804	-418.958	-333.196
594 liq	86.101	59.735	134.085	44.164	-412.598	-333.196
600	86.065	60.483	134.950	44.680	-412.445	-332.396
700	85.474	72.091	148.173	53.257	-409.927	-319.255
800	84.883	82.329	159.548	61.775	-407.469	-306.469
900	84.291	91.474	169.511	70.234	-405.087	-293.988
1000	83.700	99.728	178.361	78.633	-402.798	-281.768
1100	83.700	107.245	186.339	87.003	-400.592	-269.773
1200	83.700	114.144	193.622	95.373	-495.445	-255.513
1300	83.700	120.519	200.321	103.743	-492.507	-235.640
1400	83.700	126.443	206.524	112.113	-489.604	-215.989
1500	83.700	131.977	212.299	120.483	-486.739	-196.546
1600	83.700	137.168	217.701	128.853	-483.909	-177.294
1700	83.700	142.056	222.775	137.223	-481.110	-158.214
1800	83.700	146.674	227.559	145.593	-478.345	-139.299
1900	83.700	151.051	232.085	153.963	-475.613	-120.539
2000	83.700	155.211	236.378	162.333	-472.912	-101.921
298.15	59.530	29.246	64.430	10.490	-425.800	379.651
Uncertainties in Functions						
0	0.000	0.000	0.000	0.000	0.200	0.200
298.15 cr, $\alpha$	0.100	0.150	0.200	0.030	0.200	0.200
1000 liq	0.800	0.600	0.800	0.700	0.800	0.800
2000	5.000	3.000	5.000	5.000	5.000	6.000

### 3.2. Sodium Hydroxide in Gaseous Phase

#### 3.2.1. Sodium Hydroxide Monomer

##### Molecular Constants of NaOH

[58SPI/MAR]

Spinar and Margrave studied IR spectra of equilibrium vapors over sodium hydroxide at 890–900 °C and assigned an absorption at 433–440 cm<sup>-1</sup> to (NaOH)<sub>x</sub> where  $x = 1$  or 2. The authors [58SPI/MAR] tentatively attributed this absorption to the Na-O stretching vibration of the NaOH molecule.

[63MCB/HEI]

McBride *et al.* adopted  $\nu_1$  from [58SPI/MAR] and esti-

mated the other molecular constants of the NaOH molecule assuming a bent structure of the molecule.

[67BUE/STA] Buechler and Stauffer investigated the deflection of sodium hydroxide molecular beam in an inhomogeneous electric field at 550 °C and found that the monomer sodium hydroxide is polar.

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tric field at 550 °C and found that the monomer sodium hydroxide is polar.

[69ACQ/ABR]

Acquista and Abramowitz observed the infrared spectra of Ar matrix-isolated NaOH and NaOD. The assignment of frequencies for the  $\nu_1$  and  $\nu_2$  modes of NaOH was based on the temperature dependence of the spectral features and on the deuterium isotopic effects. In the authors' [69ACQ/ABR] opinion, the complex polymeric background made the assignment to the monomer somewhat less certain.

[73PEA/TRU]

Pearson and Trueblood observed microwave rotational transitions  $J=7\leftarrow 6$ ,  $8\leftarrow 7$ , and  $9\leftarrow 8$  in the ground vibration state of the NaOH molecule and obtained  $B_{0,0,0} = 12567.054(10)$  MHz and  $D_{0,0,0} = 0.02872(5)$  MHz.

[76KUI/TOR]

Kuijpers *et al.* measured 19 lines of the rotational transition  $J=4\leftarrow 3$  of NaOH and NaOD in a number of vibrational states. The following rotational constants for  $\nu_2$  vibration mode were obtained (in MHz):  $B_{0,e,0} = 12654(22)$ ,  $\alpha_2 = 97(20)$ ,  $\gamma_{22} = 9(2)$ , and  $\gamma_1 = -10(2)$ . The authors [76KUI/TOR] obtained the distance  $r(\text{Na-O})$  by assuming  $r(\text{O-H}) = 0.96$  Å and using the value of  $B_{0,0,0}$  (which was not given in the paper).

[79ZYU/CHA]

Zyubina and Charkin performed *ab initio* calculation of the NaOH molecular geometry.

[80NEM/STE] (see also [79NEM/STE])

Nemukhin and Stepanov applied the diatomics-in-molecules approach developed by them earlier to theoretical calculation of the ground-state equilibrium geometry and vibrational frequencies of the NaOH molecule.

[81KOZ/CAR]

Kozák and Čárský obtained the molecular constants of the NaOH molecule by the *ab initio* SCF calculation of double zeta quality. The following basis set was used: Na12s7p/7s4p, O9s5p/4s2p, and H4s/2p.

[82GUR/VEY]

Gurvich with co-workers adopted the vibrational frequencies  $\nu_1$  and  $\nu_2$  of NaOH from the IR matrix isolated spectral investigation [69ACQ/ABR]; the frequency  $\nu_3$  was estimated. The moment of inertia of NaOH was derived from the rotational constant reported in [73PEA/TRU].

[82LU1/ECK]

Lutz *et al.* measured O-H stretching frequency of solid NaOH in IR and Raman spectra.

[82PIE/FRA] (see also [82GOR/STE])

Pietro *et al.* carried out *ab initio* calculation of the geometry of the NaOH molecule using small split-valence basis set (3-21G) supplemented with d-functions (2-21G\*).

[83LON/CAP]

Long *et al.* performed *ab initio* calculation of the NaOH molecule using different basis sets and electron correlation approaches. In all approximations the molecule remained lin-

ear. The recommended constants were obtained with the 6-21G basis set and applying the Møller-Plesset perturbation theory of the third order. In this approximation  $B_{e,e,e} = 13590$  MHz. The frequencies were calculated assuming a simple valence force field. The corresponding force constants are (in CGS units)  $k_1 = 7.338 \times 10^5$ ,  $k_2 = 2.904 \times 10^5$  and  $k_\delta = 5.100 \times 10^{-13}$ .

[84RAM/ABA] (see also [79ABA/DEM], [80ABA/DEM])

Rambidi and co-workers carried out *ab initio* calculations of geometry and harmonic frequencies of NaOH. The following Gaussian atomic basis set was used: Na11s2p+2p/6s2p+2p, O9s5p/4s2p, and H9s2p/4s2p. Additionally, d-function was used for the O atom.

[85CHA/DAV]

Chase with co-workers estimated the structural parameters of NaOH assuming a linear configuration. The vibrational frequencies  $\nu_1$  and  $\nu_2$  were taken from IR study [69ACQ/ABR];  $\nu_3$  was estimated.

[86BAU/LAN]

Bauschlicher *et al.* calculated *ab initio* the values of  $r(\text{Na-O})$ ,  $\nu(\text{Na O})$ , and  $D_0(\text{Na-OH})$  for NaOH using both the self-consistent field (SCF) and singles plus doubles configuration (CISD) levels and extended Gaussian basis set of at least triple-zeta plus double polarization quality.

[86DYK/FEH]

Dyke *et al.* performed *ab initio* molecular orbital calculations for NaOH. The following Gaussian atomic basis set was used: Na6s4p, O4s2p, and H3s. This basis set was augmented by one polarization function on each center. Molecular geometry was optimized utilizing analytical gradient techniques as implemented in the GAMESS program. The force constant matrix was constructed and diagonalization of this matrix yielded vibrational frequencies for the normal modes.

[86POG/SOL] (see also [90POG])

Pogrebnaya *et al.* performed *ab initio* calculations for the NaOH molecule using MO LCAO SCF method. The geometry and harmonic frequencies of the molecule were obtained in various basis sets approximations. The molecular constants of NaOH listed in Table 3-16 were obtained with the following basis set: Na12s8p1d/6s4p1d, O9s5p/4s2p, and H5s2p/3s1p. The set for O were augmented by a polarization d-function.

[87JUG/SCH]

Jug and Schulz carried out theoretical calculations of NaOH using the SINDO1 method. The authors [87JUG/SCH] concluded the bent NaOH molecule to be more stable while linear NaOH should be considered as a transition structure with the energy about 50 kJ mol<sup>-1</sup> higher than the bent one.

#### Discussion of the Molecular Constants of NaOH(g)

The NaOH molecule in the ground electronic state ( $X^1\Sigma^+$ ) is shown to be linear by the microwave spectrum investigations [73PEA/TRU] and [76KUI/TOR]. This is supported by theoretical calculations [79ZYU/CHA, 80NEM/

TABLE 3-16. Bond lengths (in Å) and vibrational frequencies (in  $\text{cm}^{-1}$ ) of NaOH in the ground electronic state.

Reference	$r(\text{Na-O})$	$r(\text{O-H})$	$\angle(\text{Na-OH})$	$\nu_1$	$\nu_2(2)$	$\nu_3$	Note
[58SPI/MAR]	...	...	...	437	...	...	a
[69ACQ/ABR]	...	...	180	431	337	...	b
[73PEA/TRU]	1.954	0.92	180	...	...	...	c
[76KUL/TOR]	1.95	0.96	180	...	...	...	c
[79ZYU/CHA]	1.879	0.953	180	...	...	...	d
[80NEM/STE]	1.942	0.958	180	412	547	3862	e
[81COZ/CAR]	1.923	0.950	180	615	461	4120	d
[82GUR/VEY]	1.954	0.92	180	431	337	3700	f
[82PIE/FRA]	1.870	0.962	180	...	...	...	d
[83LON/CAR]	1.868	0.9805	180	710	322	3628	d
[84RAM/ABA]	1.926	0.947	180	578	409	4183	d
[85CHA/DAV]	1.93	0.97	180	431	337	3650	g
[86BAU/LAN]	1.932	...	180	579	...	...	d
[86DYK/FEH]	1.964	0.836	180	588	383	4243	d
[86POG/SOL]	1.958	0.938	180	571	325	4291	d
[87JUG/SCH]	1.917	0.948	180	...	...	...	h
[87JUG/SCH]	1.944	0.984	180	...	...	...	i
Accepted in the present work	1.954	0.92	180	540	300	3700	j

<sup>a</sup>IR spectrum of vapor.

<sup>b</sup>Matrix-isolated IR spectrum.

<sup>c</sup>Microwave spectrum.

<sup>d</sup>*Ab initio* calculation.

<sup>e</sup>Diatomics-in-molecules theoretical calculation.

<sup>f</sup>Bond lengths from [73PEA/TRU],  $\nu_1$  and  $\nu_2$  from [69ACQ/ABR],  $\nu_3$  is estimated.

<sup>g</sup>Bond lengths and  $\nu_3$  are estimated;  $\nu_1$  and  $\nu_2$  from [68ACQ/ABR].

<sup>h</sup>SINDO1 calculation for linear NaOH which is considered as a transient state with the energy about 50  $\text{kJ mol}^{-1}$ .

<sup>i</sup>SINDO1 calculation for bent ground state of NaOH with  $\angle(\text{Na-O-H})=91.6^\circ$ .

<sup>j</sup>Bond lengths from [73PEA/TRU];  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  are estimated.

STE, 81COZ/CAR, 83LON/CAR, 84RAM/ABA, 86BAU/LAN, 86DYK/FEH, 86POG/SOL]. The values of bond lengths obtained in practically all studies are in good agreement (see Table 3-16). In one semiempirical calculation [87JUG/SCH] a bent structure was obtained.

Similar to LiOH, the NaOH molecule has three fundamental frequencies:  $\nu_1$  (Na-O stretching),  $\nu_2$  (Na-O-H bending), and  $\nu_3$  (O-H stretching). The assignments of these frequencies, except  $\nu_3$ , are not firm. In the pioneer IR spectral study of gaseous alkali metal hydroxides, Spinar and Margrave [68SPI/MAR] were not able to distinguish definitely the assignment of the absorption band at 433–440  $\text{cm}^{-1}$  between either monomer or dimer of NaOH. In this connection, Acquista and Abramowitz [69ACQ/ABR] pointed out that the gas-phase measurements provided no means of differentiation between monomer and polymer absorption. These authors performed a more thorough study of the IR spectra of NaOH and NaOD in an argon matrix. Based on the temperature dependence of the relative intensities of the absorption bands and on the deuterium isotopic shifts, the authors [69ACQ/ABR] assigned the frequencies  $\nu_1$  and  $\nu_2$  for NaOH (see Table 3-16), but admitted that because of complex polymer background this assignment was somewhat uncertain. The most questionable assignment is that of the Na-O stretching frequency,  $\nu_1$ , which is more than 100  $\text{cm}^{-1}$  less than the fundamental frequency of the isoelectronic molecule NaF. It should be noted that some authors [83LON/CAP,

86BAU/LAN, 86POG/SOL, 86DYK/FEH] also doubt the value of  $\nu_1$  for NaOH found in [69ACQ/ABR]. All *ab initio* calculations yielded larger values for this frequency.

The assignment of the bending frequency ( $\nu_2$ ) of NaOH proposed in [69ACQ/ABR] is also questionable. The experimental data on the bending frequency  $\nu_2$  for alkaline-earth metal monohydroxides obtained recently (see [93GUR/VEY]) drastically changed a settled view about the decreasing of  $\nu_2$  with the increasing of the molecular mass. New spectral data on the values of  $\nu_2$  for LiOH [85MAN/LOU] (256.5  $\text{cm}^{-1}$  accepted in the present work) and for CsOH [91KON/BOO] (320  $\text{cm}^{-1}$ ) also confirm a tendency of this frequency to increase with the molecular mass. Therefore, the value of  $\nu_2$  for NaOH is presumably expected to be less than that recommended in [69ACQ/ABR].

The O-H stretching frequency of NaOH was detected neither in gas nor in matrix. Theoretical calculations yielded the value of  $\nu_3$  more or less close to a characteristic value.

For NaOH, the bond lengths are accepted on the basis of the microwave study by Pearson and Trueblood [73PEA/TRU]. The uncertainties of these values are estimated as 0.002 in  $r(\text{Na-O})$  and 0.02 in  $r(\text{O-H})$ . Corresponding (rounded) value of the moment of inertia is equal to  $(6.680 \pm 0.005)10^{-39} \text{ g cm}^2$ . On the basis of the arguments presented above, we estimate the  $\nu_1$  and  $\nu_2$  frequencies by comparing with corresponding values for alkali metal hydroxides and fluorides. The  $\nu_3$  frequency is taken to be the character-

TABLE 3-17. Differences (in  $\text{J K}^{-1} \text{mol}^{-1}$ ) between the thermal functions of  $\text{NaOH}(\text{g})$  calculated in the present work and in [82GUR/VEY, 85CHA/DAV].

<i>T</i> , K	[Present work]-[82GUR/VEY] <sup>a</sup>			[Present work]-[85CHA/DAV] <sup>b</sup>		
	$\Delta C_p^\circ(T)$	$\Delta \Phi^\circ(T)$	$\Delta S^\circ(T)$	$\Delta C_p^\circ(T)$	$\Delta \Phi^\circ(T)$	$\Delta S^\circ(T)$
298.15	-0.405	0.347	0.385	-0.405	0.489	0.531
1000	-0.078	0.231	0.103	-0.132	0.372	0.233
2000	-0.021	0.158	0.073	-0.089	0.280	0.154
3000	-0.010	0.128	0.070	-0.053	0.232	0.125
4000	-0.005	0.113	0.068	-0.033	0.204	0.113
5000	-0.003	0.106	0.068	-0.021	0.188	0.111
6000	-0.003	0.100	0.067	-0.016	0.174	0.107

<sup>a</sup>The values of  $\Phi^\circ(T)$  and  $S^\circ(T)$  tabulated in [82GUR/VEY] are recalculated to standard pressure 0.1 MPa.

<sup>b</sup>The values of  $\Phi^\circ(T)$  tabulated in [85CHA/DAV] are adjusted to the reference temperature  $T=0$  instead of 298.15 K.

istic O-H stretch. The uncertainties of the accepted values can be estimated as  $20 \text{ cm}^{-1}$  for  $\nu_1$  and  $\nu_2$  and  $100 \text{ cm}^{-1}$  for  $\nu_3$ .

For NaOH, the symmetry number  $\sigma=1$  and the statistical weight of the ground electronic state  $p_X=1$ .

The existence of low-lying excited electronic states of NaOH is not expected.

The molecular constants of NaOH adopted in the present work for calculation of the thermal functions are summarized below:

$$r(\text{Na-OH})=1.954 \pm 0.002 \text{ \AA};$$

$$r(\text{O-H})=0.92 \pm 0.02 \text{ \AA};$$

$$\angle(\text{Na-O-H})=180^\circ;$$

$$I=(6.680 \pm 0.005)10^{-39} \text{ g cm}^2;$$

$$\sigma=\text{sigma}=1;$$

$$p_X=1;$$

$$\nu_1=540 \pm 20 \text{ cm}^{-1}, d_1=1;$$

$$\nu_2=300 \pm 20 \text{ cm}^{-1}, d_2=2;$$

$$\nu_3=3700 \pm 100 \text{ cm}^{-1}, d_3=1.$$

#### Calculation of the NaOH(g) Thermal Functions

The thermal functions of  $\text{NaOH}(\text{g})$  in the standard state are calculated in the "rigid rotor-harmonic oscillator" approximation with the low-temperature quantum corrections according to the equations given in [89GUR/VEY]. The calculated values of  $C_p^\circ(T)$ ,  $\Phi^\circ(T)$ ,  $S^\circ(T)$ ,  $H^\circ(T)-H^\circ(0)$  at the temperatures 0–6000 K for  $\text{NaOH}(\text{g})$  are given in Table 3-22.

The uncertainties in the calculated thermal functions of  $\text{NaOH}(\text{g})$  are mainly due to uncertainties in the estimated fundamental frequencies, first of all  $\nu_1$  and  $\nu_2$ . Since the value of the constant of centrifugal distortion,  $D_{0,0,0}$  of NaOH is known [73PEA/TRU], it is possible to estimate the corresponding contribution to the thermal functions. It amounts to from 0.01 to 0.3  $\text{J}(\text{K mol}^{-1})$  in  $\Phi^\circ(T)$  at  $T=298.15$  and to 6000 K, respectively. At higher temperatures the uncertainties because of the approximate method of calculation become more substantial. The total uncertainties in the thermal functions of  $\text{NaOH}(\text{g})$  are presented in Table 3-22.

The thermal functions of  $\text{NaOH}(\text{g})$  were calculated earlier in [63MCB/HEI] (298.15–6000 K), [82GUR/VEY] (100–

6000 K), and [85CHA/DAV] (100–6000 K). The use of some new data in the present work results in differences of the thermal functions from those recommended in these earlier books. The comparison of these functions for  $\text{NaOH}(\text{g})$  at  $T=298.15, 1000, 2000, 3000, 4000, 5000,$  and 6000 K is shown in Table 3-17.

#### Enthalpy of formation of NaOH(g)—Experimental Determinations

##### [21WAR/ALB]

Von Wartenberg and Albrecht measured the total pressure over liquid sodium hydroxide by the boiling point method in the temperature range 1283–1681 K. The authors [21WAR/ALB] appraised the data as uncertain because of irregular character of boiling, presumably due to decomposition of condensed phase. The data are listed in Table 3-18.

##### [56MAR]

With reference to an unpublished work by L. Spinar, S. Suzuki, and J. L. Margrave (1955), the latter indicated that recent results of Knudsen effusion and flow vapor pressure methods have supported the contention of vaporization of  $\text{NaOH}(\text{g})$  molecules.

##### [58KAY/GRE]

In the study of water vapor pressures above sodium hydroxide, Kay and Gregory investigated possibility of vaporization of the hydroxide. Vaporization was not detected below  $310^\circ\text{C}$ . Considering the sensitivity of the flame photometric method, which was used for determination of total amount of sodium in vaporization products, it was concluded that the pressure of sodium hydroxide "could not be materially greater than  $10^{-8}$  atm at  $335^\circ\text{C}$ ."

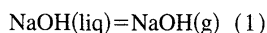
##### [58POR/SCH]

Porter and Schoonmaker carried out a mass spectrometric study of vaporization of sodium and potassium hydroxides. Effusion cells consisted of an outer metallic crucible (stainless steel or platinum) with an inner lining of magnesia. In the case of sodium hydroxide the ions  $\text{Na}^+$ ,  $\text{NaOH}^+$ , and  $\text{Na}_2\text{OH}^+$  were detected. The use of stainless steel crucibles resulted in extensive reduction of the condensed hydroxides. With platinum crucibles, reduction was diminished considerably; but even under these conditions the  $\text{Na}^+$  was the most

abundant ion in the sodium hydroxide mass spectrum. The authors [58POR/SCH] came to the conclusion that in the temperature range of measurements (270 °C–450 °C) the vapors consist largely of dimer molecules. The ratio  $\text{Na}_2\text{OH}^+/\text{NaOH}^+$  was temperature dependent. This was interpreted as an indication of formation of substantial  $\text{NaOH}^+$  ion current fraction by simple ionization of NaOH molecules.

#### [58SCH/POR]

Schoonmaker and Porter [58SCH/POR] described subsequent results of sodium hydroxide investigation by Knudsen effusion mass spectrometry (preliminary account was published in [58POR/SCH]). The data presented were obtained with the use of a platinum crucible lined with a pressed layer of magnesia. The temperature range of measurements was 300 °C–450 °C. From appearance potential measurements it followed that  $\text{Na}^+$  ions were produced by the simple ionization of free sodium atoms.  $\text{NaOH}^+$  formation was attributed to simple ionization of NaOH molecules. From two independent determinations the enthalpy of vaporization for the process:



was found:  $\Delta_r H^\circ(660 \text{ K}) = 41 \pm 3 \text{ kcal mol}^{-1}$  ( $171.5 \pm 13 \text{ kJ mol}^{-1}$ ). Using an average value  $C_p(\text{NaOH}, \text{g}) = 10 \text{ cal K}^{-1} \text{ mol}^{-1}$  the value  $\Delta_r H^\circ(298.15 \text{ K}) = 46.8 \pm 3 \text{ kcal mol}^{-1}$  ( $195.8 \pm 13 \text{ kJ mol}^{-1}$ ) was obtained.

#### [58POR/SCH2]

In a study of NaOH-KOH system Porter and Schoonmaker determined partial pressure of NaOH(g):  $2.2 \times 10^{-8} \text{ atm}$  at the temperature 666 K. Condensed phase composition was not specified. Comparison of mass spectrum of this system and of individual sodium hydroxide may lead to the conclusion that sodium hydroxide activity was not far from unity.

#### [59SCH/POR]

Schoonmaker and Porter carried out mass spectrometric study of alkali hydroxides using effusion cells constructed of platinum lined with a pressed magnesia and cells of pure silver. In the case of silver effusion cells, the degree of reduction of condensed hydroxide was diminished substantially, and the authors [59SCH/POR] concluded that under these experimental conditions the major portion of  $\text{M}^+$  ions was formed by dissociative ionization of MOH molecules. They discussed apparent reduction in the activity of molten alkali hydroxides in the presence of magnesia and indicated the necessity of the reappraisal of thermodynamic data previously reported for the vaporization of sodium hydroxide [58SCH/POR].

#### [60SCH/POR]

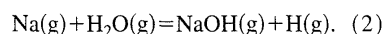
Schoonmaker and Porter detected  $\text{Na}^+$ ,  $\text{NaOH}^+$ ,  $\text{Na}_2\text{O}^+$ , and  $\text{Na}_2\text{OH}^+$  ions in mass spectra of the system  $\text{Na}_2\text{O}(\text{cr})\text{-H}_2\text{O}(\text{g})$ . Studies were conducted in the temperature range 534–886 °C. In one run at 811 °C  $\text{Na}_3(\text{OH})_2^+$  ions were detected as well, with the ratio  $\text{NaOH}^+:\text{Na}_2\text{OH}^+:\text{Na}_3(\text{OH})_2^+ = 1:2:0.07$ . The formation of  $\text{NaOH}^+$  ions was ascribed to monomer,  $\text{Na}_2\text{O}^+$  and  $\text{Na}_2\text{OH}^+$ -to dimer, and  $\text{Na}_3(\text{OH})_2^+$  to trimer molecules.

#### [60RAO/SCH]

Rao and Schoonmaker used the molecular beam velocity selector to study vapor composition of sodium hydroxide. The ovens with narrow slits were made of silver. In several runs where beam deflecting magnets were utilized, the total beam intensity was independent of magnet field gradient, thus indicating absence of substantial amounts of free atomic sodium in molecular beam. The results of runs at different temperatures and with different ovens show large scatter. Observation of ovens after several series of runs always revealed a surface layer of hydroxide on the external slit faces. Thus the molecular beam represented a composite of molecules effusing from the oven aperture and from the slit faces. As a typical result of measurements, Rao and Schoonmaker indicated partial pressures of monomer and dimer at the temperature 936 K,  $1.0 \times 10^{-3}$  and  $2.9 \times 10^{-3} \text{ mm Hg}$ , respectively. Details of calculation of partial pressures were not presented.

#### [66JEN/PAD], [70JEN]

Jensen and Padley performed measurements of sodium hydroxide formation in  $\text{H}_2 + \text{O}_2 + \text{N}_2$  flames (see Section 2.2.1 for details). It was found that the logarithmic plot of D-line emission intensity against  $1/T$  had some deviation from linearity at the temperatures exceeding 2300 K. Part of this deviation was caused by formation of  $\text{Na}^+$  ions. Ionization of sodium atoms was suppressed by means of addition of a high concentration of cesium chloride to the atomizer solution of dilute sodium chloride. Remaining deviation from linearity was attributed to presence of NaOH molecules. For the principal flame with the temperature  $T = 2475 \pm 15 \text{ K}$ , the value  $[\text{NaOH}]/[\text{Na}] = 0.08 \pm 0.03$  was calculated. To this value corresponded the equilibrium constant value  $K^\circ(2475) = 2.5 \cdot 10^{-3}$  for the reaction



Third-law calculation performed in [66JEN/PAD] using a bent hydroxide molecule model resulted in the value  $D_0(\text{Na-OH}) = 77 \pm 4 \text{ kcal mol}^{-1}$  ( $322 \pm 17 \text{ kJ mol}^{-1}$ ).

Jensen [70JEN] recalculated the data from [66JEN/PAD] using a linear model of NaOH molecule and recommended the value  $D_0(\text{Na-OH}) = 325 \pm 16 \text{ kJ mol}^{-1}$ .

#### [69COT/JEN]

For determination of the bond dissociation energy of the alkali metal hydroxides, Cotton and Jenkins used a method based on the measurements of alkali metal concentration as a function of hydrogen atom concentration in hydrogen rich  $\text{H}_2 + \text{O}_2 + \text{N}_2$  flames of different composition of unburnt gases (see Section 2.2.1). As indicated on the page 1540 of the paper [69COT/JEN], flames at 2030 K were used for sodium. However, in Table 3 (page 1542) results of calculations of  $D_0(\text{Na-OH})$  also for a set of six flames with the temperature 1800 K were presented. The mean value of equilibrium constant for reaction (2) from six flames at  $T = 2030 \text{ K}$  was given:  $K^\circ = 8.5 \times 10^{-4}$  (the values of equilibrium constant for individual flames were not presented).

Cotton and Jenkins performed the third-law calculations of  $D_0(\text{Na-OH})$  for each flame in both sets with the use of aux-

iliary data from JANAF tables (see [71STU/PRO]). Average value of  $D_0(\text{Na-OH})$  for the flame with the temperature 2030 K is  $80.75 \pm 0.72 \text{ kcal mol}^{-1}$  or  $337.9 \pm 3.0 \text{ kJ mol}^{-1}$  (error bars represent standard deviation). As the best value of the dissociation energy together with the total error limit Cotton and Jenkins recommended  $D_0(\text{Na-OH}) = 80 \pm 2 \text{ kcal mol}^{-1}$  ( $335 \pm 8 \text{ kJ mol}^{-1}$ ).

[71KEL/PAD]

Kelly and Padley conducted photometric studies of Na emission in  $\text{H}_2 + \text{O}_2 + \text{CO}_2$  and  $\text{H}_2 + \text{O}_2 + \text{N}_2$  flames in the temperature range 1950–2750 K. Exactly 32 values of equilibrium constant for reaction (2) were obtained. The data were presented on the graph. Kelly and Padley fitted the equilibrium constant values as the function of T in the temperature range 1950–2750 K with the equation

$$K^\circ(T) = A \exp(-\Delta_f H^\circ(2350 \text{ K})/RT),$$

where  $\log A = 1.52$ ,  $\Delta_f H^\circ(2350 \text{ K}) = 189 \text{ kJ mol}^{-1}$ .

From the enthalpy of reaction (2) for the mean temperature of measurements  $T = 2350 \text{ K}$ , Kelly and Padley calculated the values of  $D_0(\text{Na-OH})$  for linear and bent models of the molecule:  $330 \pm 8 \text{ kJ mol}^{-1}$  (second law, linear);  $330 \text{ kJ mol}^{-1}$  (third law, linear);  $323 \text{ kJ mol}^{-1}$  (second law, bent);  $313 \text{ kJ mol}^{-1}$  (third law, bent).

They recommended as the best the value  $D_0(\text{Na-OH}) = 330 \text{ kJ mol}^{-1}$  based on the second law treatment for the linear model.

The equation given permits to calculate the following values of  $K^\circ$  for reaction (2) at the lowest, mean and highest temperature of the range: 1950 K,  $K^\circ = 2.86 \times 10^{-4}$ ; 2350 K,  $K^\circ = 2.08 \times 10^{-3}$ ; 2750 K,  $K^\circ = 8.51 \times 10^{-3}$ . These values were used by the authors of this review for third law calculation of the enthalpy of reaction (2).

[84DEV/CAR]

Dever, Cardelino, and Gole obtained chemiluminescent electronic spectrum of  $\text{NaOH}(\text{g})$  in a study of  $\text{Na}_2 + \text{H}_2\text{O}_2$  diffusion flame. From the short-wavelength (3465 Å) limit of the continuous spectrum they found a lower limit for the dissociation energy:  $D_0(\text{Na-OH}) \geq 82.5 \text{ kcal mol}^{-1}$  ( $345 \text{ kJ mol}^{-1}$ ).

[84HYN/STE]

Hynes, Steinberg, and Schofield performed detailed study of sodium and hydroxyl concentration in ten oxygen-rich  $\text{H}_2\text{-O}_2\text{-N}_2$  flames. From a kinetic analysis of sodium distribution within the highest temperature, low oxygen flame, in which NaOH had the highest concentration and was equilibrated, they concluded that their results supported the value  $D_0(\text{Na-OH}) = 78.9 \pm 2 \text{ kcal mol}^{-1}$  ( $330 \pm 8 \text{ kJ mol}^{-1}$ ), recommended by Kelly and Padley [71KEL/PAD].

Enthalpy of Formation of NaOH(g)—Calculations

[81KOZ/CAR]

Kozák and Carsky calculated the energy change for the reaction:



Applying zero-point correction,  $-24.9 \text{ kJ mol}^{-1}$  (calculated by the authors of this paper with the use of accepted frequen-

cies for NaOH molecule), we obtain slightly rounded value  $\Delta_f H^\circ(0) = 145 \text{ kJ mol}^{-1}$ . The enthalpy of formation  $\Delta_f H^\circ(\text{NaOH}, \text{g}, 0) = -202 \text{ kJ mol}^{-1}$  and dissociation energy  $D_0(\text{Na-OH}) = 349 \text{ kJ mol}^{-1}$  correspond to this value.

[86BAU/LAN]

Bauschlicher Jr. *et al.* calculated the value  $D_e(\text{Na}^+ \cdot \text{OH}^-)$ , from which the value  $D_0(\text{Na-OH}) = 3.51 \pm 0.10 \text{ eV}$  ( $338 \pm 10 \text{ kJ mol}^{-1}$ ) was found, with zero-point correction  $D_e(\text{Na-OH}) - D_0(\text{Na-OH}) = 0.08 \text{ eV}$ . To this value corresponds the enthalpy of formation  $\Delta_f H^\circ(\text{NaOH}, \text{g}, 0) = -191 \pm 10 \text{ kJ mol}^{-1}$ .

[91CUR/RAG], see also [89POP/HEA]

Curtiss, Raghavachari, Trucks, and Pople calculated the atomization energy of the NaOH molecule using composite Gaussian-1 and Gaussian 2 *ab initio* theoretical procedures, utilizing large basis sets and treating electron correlation by Möller–Plesset perturbation theory and by quadratic configuration interaction (see Section 2.2.1). For the NaOH the following atomization enthalpies were obtained: Gaussian-1,  $185.5 \text{ kcal mol}^{-1}$  ( $776.1 \text{ kJ mol}^{-1}$ ); Gaussian-2,  $182.1 \text{ kcal mol}^{-1}$  ( $761.9 \text{ kJ mol}^{-1}$ ). The following enthalpy of formation values,  $\Delta_f H^\circ(\text{NaOH}, \text{g}, 0)$ , correspond to these values: Gaussian-1,  $-205.5 \text{ kJ mol}^{-1}$ ; Gaussian-2,  $-191.3 \text{ kJ mol}^{-1}$  (calculated using enthalpies of formation for Na(g) from [82GUR/VEI] and for O(g) and H(g) from [89GUR/VEI]).

The total energy values presented in [91CUR/RAG] make it possible to calculate from these data dissociation energies  $D_0(\text{Na-OH})$  and  $D_0(\text{Na}^+ \cdot \text{OH}^-)$ ,  $\text{kJ mol}^{-1}$ :

Gaussian-1,  $D_0(\text{Na-OH}) = 356.0$ ,  $D_0(\text{Na}^+ \cdot \text{OH}^-) = 655.5$ ;  
Gaussian-2,  $D_0(\text{Na-OH}) = 337.1$ ,  $D_0(\text{Na}^+ \cdot \text{OH}^-) = 633.8$ .

The following  $\Delta_f H^\circ(\text{NaOH}, \text{g}, 0)$  values correspond to dissociation energies listed:

Gaussian-1,  $-209.1$  and  $-188.9$ , respectively;  
Gaussian-2,  $-190.2$  and  $-167.2$ , respectively.

Discussion of the Enthalpy of Formation of NaOH(g)

The equilibrium constant values from the papers annotated above have been recalculated with the accepted thermal functions and auxiliary data from [82GUR/VEY] and [89GUR/VEY]. The recalculated values of enthalpies of reactions and the values of enthalpy of formation of NaOH(g) are collected in Table 3-19. For the enthalpies of reactions, errors represent statistical uncertainty (95% confidence level). For the enthalpy of formation, error assessment represents a total uncertainty estimate (see Section 2.2.1 for details).

In contrast to lithium hydroxide, the degree of decomposition of sodium hydroxide at elevated temperatures (e.g. in the temperature range of mass spectrometric measurements) is low. In this case the most reliable enthalpy of formation value of NaOH(g) can be obtained from the combination of the enthalpy of formation for solid with the enthalpy of sublimation. However, the data which can be used for evaluation of enthalpy of sublimation are scarce and contradictory. The data of von Wartenberg and Albrecht [21WAR/ALB] are

uncertain, as was mentioned earlier, and represent total pressure of vapor over molten sodium hydroxide. In particular, there is no smooth dependence of  $\log P$  vs  $1/T$  (see Fig. 3-5.); rather it is stepwise. Information on vapor pressure composition is necessary for interpretation of data from [21WAR/ALB]. Mass spectrometric data obtained in a series of works by Porter and Schoonmaker (see above) are mainly qualitative. There are two reasons for lack of quantitative data for sodium hydroxide: indefinite composition of condensed phase ([59SCH/POR]) and creeping of the molten hydroxide to the outer side of effusion cells. The latter phenomenon, detected by Rao and Schoonmaker ([60RAO/SCH]) evidently resulted in a substantial increase of effective evaporating area in comparison with the area of effusion orifice in the mass spectrometric studies. From this we may conclude that the monomer and dimer vapor pressures at the temperature 666 K, given in [58POR/SCH2], are seriously overestimated. On the other hand, we may suppose, that the vapor pressure values for monomer and dimer given in the paper by Rao and Schoonmaker ([60RAO/SCH]) are essentially free from this error.

Dever *et al.* [84DEV/CAR] deduced the value  $D_0(\text{Na-OH}) > 345 \text{ kJ mol}^{-1}$  from a preliminary analysis of  $\text{Na}_2\text{-H}_2\text{O}_2$  system emission spectrum. This value corresponds to the enthalpy of formation value  $\Delta_f H^\circ(\text{NaOH}, \text{g}, 0) \leq -198$

$\text{kJ mol}^{-1}$ . Without a detailed analysis of the spectrum we do not regard results of this work as a reliable source of information on the stability of NaOH molecule.

The most reliable data for evaluation of the NaOH(g) enthalpy of formation are obtained in flame photometric studies [66JEN/PAD], [69COT/JEN], and [71KEL/PAD]. Results of these studies are in reasonable agreement.

Results of quantum mechanical calculations are presented in Table 3-20. The data from the most advanced studies [86BAU/LAN] and [91CUR/HEA] are in agreement with the flame photometric results.

On the basis of cited flame photometric works ([66JEN/PAD], [69COT/JEN], and [71KEL/PAD]) we adopt the value

$$\Delta_f H^\circ(\text{NaOH}, \text{g}, 298.15 \text{ K}) = -191.0 \pm 8 \text{ kJ mol}^{-1}.$$

The adopted value is obtained as slightly rounded weighted average; error assessment represent the total error estimate. Comparison with enthalpies of formation from other critical reviews is given in Table 3-21.

### 3.2.2. Appendix. Tables of Experimental and Evaluated Data for NaOH(g)

TABLE 3-18. Vapor pressure of sodium hydroxide, [21WAR/ALB].

No.	T/K	P/mm Hg	No.	T/K	P/mm Hg
1	1283	69	11	1571	531.3
2	1361	69	12	1600	529.2
3	1441	249.2	13	1608	526.5
4	1447	132.1	14	1612	519
5	1450	148.5	15	1631	759.6
6	1491	259.2	16	1648	760.8
7	1495	291	17	1657	757.5
8	1504	269	18	1675	762.1
9	1511	265.4	19	1681	759.5
10	1564	536.9			

TABLE 3-19. Results of experimental determinations of  $\Delta_f H^\circ(\text{NaOH}, \text{g}, 0)$ ,  $\text{kJ mol}^{-1}$ .

Reference	Method	$\Delta_f H^\circ(0)$		$\Delta_f H^\circ(0)$ Third law
		Second law	Third law	
[58SCH/POR]	Knudsen effusion mass spectrometry, NaOH(liq)=NaOH(g), 573–723 K, 2 sets of measurements	193±13	...	-228±13
[58POR/SCH2]	Knudsen effusion mass spectrometry NaOH(liq)=NaOH(g), 666 K (1 point)	...	201.2	-220±20
[60RAO/SCH]	Intensity of molecular beam in a molecular beam velocity selector, NaOH(liq)=NaOH(g), 936 K (1 point)	...	241.5	-179.8±10
[66JEN/PAD]	Flame photometry, Na(g)+H <sub>2</sub> O(g)=NaOH(g)+H(g), 2475 K (1 point)	...	168.0	-179.2±8
[69COT/JEN]	Flame photometry, Na(g)+H <sub>2</sub> O(g)=NaOH(g)+H(g), 2030 K (6 points)	...	151.8±6	-195.4±9
[71KEL/PAD]	Flame photometry, Na(g)+H <sub>2</sub> O(g)=NaOH(g)+H(g), 1950–2750 K (33 points)	165.2	162.0±1.4	-185.2±2
[84DEV/CAR]	Emission spectroscopy			≤ -198



TABLE 3-20. Results of quantum-mechanical calculations of  $\Delta_f H^\circ(\text{NaOH,g,0})$ ,  $\text{kJ mol}^{-1}$ .

Reference	$\Delta_f H^\circ(\text{NaOH,g,0})$
[81KOZ/CAR]	-202
[86BAU/LAN]	-191±10
[91CUR/HEA]	-191.3 <sup>a</sup> -190.2 <sup>b</sup> -167.2 <sup>c</sup>

<sup>a</sup>From  $\Sigma D_0$ , Gaussian-2 (see the text).<sup>b</sup>From  $D_0(\text{Na-OH})$ , Gaussian-2.<sup>c</sup>From  $D_0(\text{Na}^+ - \text{OH}^-)$ , Gaussian-2.

TABLE 3-21. Comparison of the heat capacity, enthalpy, entropy, and enthalpy of formation values for NaOH(g).

Reference	$C_p^\circ$ (298.15 K)	$S^\circ$ (298.15 K)	$H^\circ(298.15 \text{ K}) - H^\circ(0)$	$\Delta_f H^\circ$ (298.15 K)
	$\text{J K}^{-1} \text{ mol}^{-1}$	$\text{J K}^{-1} \text{ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$
82MED/BER	48.5	228.4	11.38	-187.4±12
82WAG/EVA	48.37	228.43	11.38	-207.1
82GUR/VEY	48.371	228.589	11.386	-185.6±10
85CHA/DAV	48.371	228.443	11.385	-197.8±12.6
Adopted	47.966	228.975	11.396	-191±8

TABLE 3-22. Thermodynamic properties at 0.1 MPa: NaOH(g).

T(K)	$C_p^\circ$	$-(G^\circ - H^\circ(0))/T$	$S^\circ$	$H^\circ - H^\circ(0)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
	$\text{J (mol K)}^{-1}$			$\text{kJ mol}^{-1}$		
0	0.000	0.000	0.000	0.000	-187.362	-187.362
25	29.101	113.588	142.621	0.726	-187.307	-188.458
50	29.322	133.728	162.821	1.455	-187.672	-189.532
75	30.884	145.566	174.951	2.204	-188.181	-190.352
100	33.561	154.106	184.189	3.008	-188.651	-191.003
150	39.071	166.683	198.870	4.828	-189.419	-192.006
200	43.228	176.256	210.715	6.892	-190.025	-192.771
250	46.082	184.172	220.688	9.129	-190.542	-193.399
300	48.026	190.990	229.272	11.485	-191.017	-193.929
350	49.375	197.007	236.783	13.922	-191.496	-194.377
400	50.337	202.403	243.442	16.416	-194.644	-194.548
450	51.044	207.300	249.414	18.951	-195.163	-194.504
500	51.582	211.786	254.821	21.517	-195.643	-194.405
600	52.366	219.771	264.299	26.717	-196.514	-194.075
700	52.963	226.726	272.418	31.985	-197.305	-193.605
800	53.498	232.890	279.525	37.308	-198.042	-193.024
900	54.021	238.430	285.857	42.684	-198.743	-192.355
1000	54.543	243.463	291.575	48.112	-199.425	-191.609
1100	55.060	248.078	296.798	53.592	-200.109	-190.795
1200	55.566	252.341	301.611	59.124	-200.800	-187.456
1300	56.051	256.305	306.078	64.705	-201.490	-178.268
1400	56.509	260.011	310.248	70.333	-202.180	-169.090
1500	56.939	263.492	314.162	76.006	-202.870	-159.925
1600	57.336	266.775	317.850	81.720	-203.560	-150.771
1700	57.703	269.883	321.337	87.472	-204.250	-141.626
1800	58.040	272.834	324.645	93.259	-204.940	-132.493
1900	58.348	275.644	327.791	99.079	-205.630	-123.372
2000	58.630	278.327	330.791	104.928	-206.320	-114.259
2200	59.122	283.355	336.403	116.705	-207.710	-96.059
2400	59.532	287.994	341.565	128.571	-209.100	-77.892
2600	59.875	292.301	346.344	140.513	-210.490	-59.749
2800	60.163	296.322	350.793	152.518	-211.880	-41.624
3000	60.407	300.093	354.952	164.576	-213.270	-23.514
3200	60.614	303.645	358.857	176.678	-214.660	-5.415
3400	60.791	307.003	362.537	188.819	-216.050	12.682
3600	60.944	310.185	366.017	200.993	-217.440	30.790
3800	61.076	313.211	369.315	213.195	-218.830	48.902
4000	61.191	316.096	372.451	225.422	-220.220	67.029
4200	61.291	318.851	375.439	237.671	-221.610	85.183
4400	61.318	321.488	378.488	249.937	-223.000	103.359
4600	61.458	324.018	381.023	262.221	-224.390	121.571
4800	61.527	326.448	383.640	274.520	-225.780	139.817
5000	61.589	328.786	386.153	286.832	-227.170	158.113
5200	61.644	331.039	388.569	299.155	-228.560	176.453
5400	61.694	333.214	390.897	311.489	-229.950	194.839
5600	61.738	335.314	393.141	323.832	-231.340	213.291
5800	61.779	337.346	395.308	336.184	-232.730	231.802
6000	61.815	339.313	397.403	348.544	-234.120	250.377
298.15	47.966	190.753	228.975	11.396	-191.000	-193.910

## Uncertainties in Functions

0	0.000	0.000	0.000	0.000	8.000	8.000
298.15	0.500	0.700	1.200	0.150	8.000	8.000
1000	0.800	1.000	1.400	0.400	8.000	8.000
2000	1.000	1.200	1.600	0.800	8.000	8.000
3000	1.200	1.500	1.800	1.000	8.000	8.000
4000	1.500	1.800	2.200	1.500	8.000	9.000
5000	1.800	2.100	2.600	2.000	9.000	11.000
6000	2.000	2.500	3.000	2.500	9.000	15.000

## 3.2.3. Sodium Hydroxide Dimer

Molecular constants of Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub>

[58SPI/MAR]

Spinar and Margrave studied IR spectra of equilibrium vapors over sodium hydroxide at 890–900 °C and assigned an absorption at 433–440 cm<sup>-1</sup> to (NaOH)<sub>x</sub> where x=1 or 2. The authors [58SPI/MAR] tentatively attributed this absorption to Na-O stretching vibration of the monomer (Tables 3-23 and 3-24).

[63MCB/HEI]

McBride *et al.* estimated molecular constants of the Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub> molecule assuming nonplanar configuration (C<sub>2h</sub> symmetry).

[67BUE/STA]

Buechler and Stauffer investigated the deflection of sodium hydroxide molecular beam in an inhomogeneous electric field at 550 °C and found that the dimer, Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub> is nonpolar. The authors [67BUE/STA] concluded that the Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub> molecule has planar rhomboid configuration at least for the Na<sub>2</sub>O<sub>2</sub> fragment of the molecule.

[69ACQ/ABR]

Acquista and Abramowitz observed the infrared spectra of the Ar matrix-isolated NaOH and NaOD molecules. The assignment of frequencies for the ν<sub>1</sub> and ν<sub>2</sub> modes in NaOH was based on the temperature dependence of the spectral features and on the deuterium isotopic effects. In the authors' [69ACQ/ABR] opinion, the complex polymeric background in the case of NaOH made the assignment somewhat less certain.

[82GUR/VEY]

Gurvich with co-workers estimated all molecular constants of Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub> by comparison with similar molecules (the other alkali hydroxide dimers and alkali fluoride dimers) assuming D<sub>2h</sub> symmetry.

[85CHA/DAV]

Chase with co-workers estimated all molecular constants of Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub>. In accordance with the conclusions made in [60BER/MES] and [67BUE/STA], the molecular configuration of Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub> was assumed to consist of a square planar

TABLE 3-23. Bond lengths (in Å), angles (in °), and vibrational frequencies (in cm<sup>-1</sup>) of Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub> in the ground electronic state.

Constants	[82GUR/VEY] <sup>a</sup>	[85CHA/DAV] <sup>a</sup>	Accepted in the present work
r(Na-O)	2.12	2.17	2.1
r(O-H)	0.97	0.96	0.97
<(O-Na-O)	100	90	85
<i>trans</i>	0	110	0
out-of-plane <(nA-O-H)			
ν <sub>1</sub>	3700 (A <sub>g</sub> )	3700	3700 (A <sub>g</sub> )
ν <sub>2</sub>	450 (A <sub>g</sub> )	350	500 (A <sub>g</sub> )
ν <sub>3</sub>	230 (A <sub>g</sub> )	209	250 (A <sub>g</sub> )
ν <sub>4</sub>	310 (B <sub>2g</sub> )	1250	500 (B <sub>2g</sub> )
ν <sub>5</sub>	300 (B <sub>3g</sub> )	270	400 (B <sub>3g</sub> )
ν <sub>6</sub>	300 (B <sub>3g</sub> )	1250	300 (B <sub>3g</sub> )
ν <sub>7</sub>	190 (B <sub>1u</sub> )	201	200 (B <sub>1u</sub> )
ν <sub>8</sub>	300 (B <sub>1u</sub> )	1250	300 (B <sub>1u</sub> )
ν <sub>9</sub>	300 (B <sub>2u</sub> )	1250	350 (B <sub>2u</sub> )
ν <sub>10</sub>	320 (B <sub>2u</sub> )	313	350 (B <sub>2u</sub> )
ν <sub>11</sub>	3700 (B <sub>3u</sub> )	3700	3700 (B <sub>3u</sub> )
ν <sub>12</sub>	390 (B <sub>3u</sub> )	294	500 (B <sub>3u</sub> )
Symmetry	D <sub>2h</sub>	C <sub>2h</sub>	D <sub>2h</sub>

<sup>a</sup>Estimated.

Na<sub>2</sub>O<sub>2</sub> part with the hydrogen atoms in *trans* positions above and below the plane (C symmetry). The structural parameters were estimated. The six vibrational frequencies belonging to Na<sub>2</sub>O<sub>2</sub> part were estimated by comparison with corresponding frequencies of alkali metal fluorides and hydroxides. The remaining OH frequencies were taken from [60BER/MES] where they were estimated for Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>.

Discussion and Selection of the Molecular Constants of Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub>

Spectral studies or theoretical calculations of molecular constants of sodium hydroxide dimer, Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub>, have not been reported in the literature. The data available [63MCB/HEI, 82GUR/VEY, 85CHA/DAV] are empirical estimations. By analogy with Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub> and the other alkali metal dihydroxide, it is assumed that the D<sub>2h</sub> configuration of Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub> assumed in [82GUR/VEY] is more probable than C<sub>2h</sub> configuration accepted in [85CHA/DAV]. The description of the vibrational modes for Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub> is similar to that for Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub> (see Part 3.2).

TABLE 3-24. Differences (in J K<sup>-1</sup> mol<sup>-1</sup>) between the thermal functions of Na<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g) calculated in the present work and in [82GUR/VEY, 85CHA/DAV].

T, K	[Present work]-[82GUR/VEY] <sup>a</sup>			[Present work]-[85CHA/DAV] <sup>b</sup>		
	ΔC <sub>p</sub> <sup>o</sup> (T)	ΔΦ <sup>o</sup> (T)	ΔS <sup>o</sup> (T)	ΔC <sub>p</sub> <sup>o</sup> (T)	ΔΦ <sup>o</sup> (T)	ΔS <sup>o</sup> (T)
298.15	-4.875	-4.527	-9.520	18.075	4.488	2.371
1000	-0.603	-9.415	-12.146	6.318	8.313	15.049
2000	-0.154	-10.857	-12.375	1.807	14.513	21.583
3000	-0.069	-11.371	-12.418	0.823	16.971	22.092
4000	-0.037	-11.636	-12.434	0.467	18.276	22.272
5000	-0.024	-11.792	-12.436	0.251	19.089	22.367
6000	-0.011	-11.900	-12.440	0.210	19.538	22.407

<sup>a</sup>The values of Φ<sup>o</sup>(T) and S<sup>o</sup>(T) tabulated in [82GUR/VEY] are recalculated to standard pressure 0.1 MPa.<sup>b</sup>The values of Φ<sup>o</sup>(T) tabulated in [85CHA/DAV] are adjusted to the reference temperature T=0 instead of 298.15 K.

The estimates of the molecular constants of  $\text{Na}_2\text{O}_2\text{H}_2$  were made from the comparison of structural parameters and vibrational frequencies in the other dimers of alkali metal hydroxides taking into account that the values of the frequencies attributed in [69ACQ/ABR] to monomer actually may belong to the dimer. The uncertainties of the structural parameters are estimated as 0.02 Å in the bond lengths and about 3° in the  $\angle(\text{O-Na-O})$ . Corresponding value of the product of principal moments of inertia is  $(7000 \pm 5000) 10^{-117} \text{ g}^3 \text{ cm}^6$ . The uncertainties in the accepted values of the fundamental frequencies amount to 10%.

For  $\text{Na}_2\text{O}_2\text{H}_2$  the symmetry number  $\sigma=4$ , and the statistical weight of the ground electronic state  $p_X=1$ .

The existence of low-lying excited electronic states of  $\text{Na}_2\text{O}_2\text{H}_2$  is not expected.

The molecular constants of  $\text{Na}_2\text{O}_2\text{H}_2$  accepted in the present work for calculation of thermal functions are summarized below:

$$\begin{aligned} r(\text{Na-OH}) &= 2.10 \pm 0.02 \text{ \AA}, \\ r(\text{O-H}) &= 0.97 \pm 0.02 \text{ \AA}, \\ \angle(\text{O-Na-O}) &= 85 \pm 3^\circ, \\ I_A I_B I_C &= (7000 \pm 500) \times 10^{-117} \text{ g}^3 \text{ cm}^6, \\ \sigma &= \text{sigma}=4, \\ p_X &= 1, \\ \nu_1 &= 3700 \pm 100 \text{ cm}^{-1}, d_1 = 1; \\ \nu_2 &= 500 \pm 50 \text{ cm}^{-1}, d_2 = 1; \\ \nu_3 &= 250 \pm 25 \text{ cm}^{-1}, d_3 = 1; \\ \nu_4 &= 500 \pm 50 \text{ cm}^{-1}, d_4 = 1; \\ \nu_5 &= 400 \pm 40 \text{ cm}^{-1}, d_5 = 1; \\ \nu_6 &= 300 \pm 30 \text{ cm}^{-1}, d_6 = 1; \\ \nu_7 &= 200 \pm 20 \text{ cm}^{-1}, d_7 = 1; \\ \nu_8 &= 300 \pm 30 \text{ cm}^{-1}, d_8 = 1; \\ \nu_9 &= 350 \pm 35 \text{ cm}^{-1}, d_9 = 1; \\ \nu_{10} &= 350 \pm 35 \text{ cm}^{-1}, d_{10} = 1; \\ \nu_{11} &= 3700 \pm 100 \text{ cm}^{-1}, d_{11} = 1; \\ \nu_{12} &= 500 \pm 50 \text{ cm}^{-1}, d_{12} = 1. \end{aligned}$$

#### Calculation of the $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$ Thermal Functions

The thermal functions of  $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$  in the standard state are calculated in the "rigid rotor-harmonic oscillator" approximation with the low-temperature quantum corrections according to the equations given in [93GUR/VEY]. The calculated values of  $C_p^\circ(T)$ ,  $\Phi^\circ(T)$ ,  $S^\circ(T)$ ,  $H^\circ(T) - H^\circ(0)$  at the temperatures 0–6000 K are given in Table 3-27.

The uncertainties in the calculated thermal functions of  $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$  are from uncertainties in all estimated molecular

constants. At higher temperatures the uncertainties because of the approximate method of calculation become substantial. The total uncertainties in the thermal functions of  $\text{Na}_2\text{O}_2\text{H}_2$  are presented in Table 3-27.

The thermal functions of  $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$  were calculated earlier in [63MCB/HEI] (298.15–6000 K), [82GUR/VEY] (100–6000 K), and [85CHA/DAV] (100–6000 K). The use of some new data in the present work results in differences of the thermal functions from those recommended in these books. The comparison of these functions for  $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$  at  $T=298.15, 1000, 2000, 3000, 4000, 5000,$  and 6000 K are shown in Table 3-24.

#### Enthalpy of Formation of $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$ —Experimental Determinations

[58POR/SCH], [58SCH/POR], [58POR/SCH2], [60SCH/POR]

Porter and Schoonmaker published a series of papers concerning mass spectrometric studies of evaporation of alkali hydroxides. The data for the dimer vaporization are presented below.

The second-law enthalpy of vaporization of dimer and dimerization enthalpy of monomer for the mean temperature 660 K are given in the paper [58SCH/POR]:  $28 \pm 3 \text{ kcal mol}^{-1}$  ( $117 \pm 13 \text{ kJ mol}^{-1}$ ) and  $-54 \pm 5 \text{ kcal mol}^{-1}$  ( $226 \pm 21 \text{ kJ mol}^{-1}$ ), respectively.

The value  $P(\text{Na}_2\text{O}_2\text{H}_2) = 1.3 \times 10^{-7} \text{ atm}$  ( $T=666 \text{ K}$ ) is given in [58POR/SCH2] for the system NaOH-KOH with an activity of NaOH not far from unity.

[60RAO/SCH]

Rao and Schoonmaker [60RAO/SCH] determined the partial pressures of monomer and dimer in the course of vapor composition study with the molecular beam velocity selector. For the dimer they give the value  $P(\text{Na}_2\text{O}_2\text{H}_2) = 2.9 \times 10^{-3} \text{ mm Hg}$  ( $T=936 \text{ K}$ ).

#### Discussion of the Enthalpy of Formation Data

The data from the papers annotated above were recalculated with the use of thermal functions and thermochemical values adopted in this review and with auxiliary data from reference books [82GUR/VEI] and [89GUR/VEI]. The results are collected in Table 3-25.

From the analysis of papers listed above follows that in most cases the data are uncertain due to unknown condensed phase composition and influence of creeping of the molten

#### 3.2.4. Appendix. Tables of Experimental and Evaluated Data for $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$

TABLE 3-25. Results of determinations of  $\Delta_f H^\circ(\text{Na}_2\text{O}_2\text{H}_2, \text{g}, 0)$ ,  $\text{kJ mol}^{-1}$ .

Reference	Method	$\Delta_f H^\circ(0)$		$\Delta_f H^\circ(0)$ (Third law)
		(Second law)	(Third law)	
58SCH/POR	Knudsen effusion mass spectrometry, $2\text{NaOH}(\text{liq}) = \text{Na}_2\text{O}_2\text{H}_2(\text{g})$ 573–723 K (2 sets of measurements)	$159 \pm 13$	...	...
58POR/SCH2	Knudsen effusion mass spectrometry, $2\text{NaOH}(\text{liq}) = \text{Na}_2\text{O}_2\text{H}_2(\text{g})$ , 666 K (1 point)	...	201.1	$-641 \pm 20$
60RAO/SCH	Molecular beam velocity selector, $2\text{NaOH}(\text{liq}) = \text{Na}_2\text{O}_2\text{H}_2(\text{g})$ , 936 K (1 point)	...	236.6	$-613 \pm 10$

TABLE 3-26. Comparison of the heat capacity, enthalpy, entropy, and enthalpy of formation values for  $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$ .

Reference	$C_p^\circ$	$S^\circ$	$H^\circ(298.15 \text{ K}) -$	$\Delta_f H^\circ$
	(298.15 K)	(298.15 K)	$H^\circ(0)$	(298.15 K)
	$\text{J K}^{-1} \text{ mol}^{-1}$		$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$
82MED/BER	102.2	319.2	20.84	$-590.8 \pm 25$
82WAG/EVA	79.1	306	17.32	-628
82GUR/VEY	102.234	319.287	20.835	$-589.2 \pm 25$
85CHA/DAV	79.284	307.396	17.301	$-607.5 \pm 25.1$
Adopted	97.360	309.769	19.346	$-624 \pm 10$

TABLE 3-27. Thermodynamic properties at 0.1 MPa:  $\text{Na}_2\text{O}_2\text{H}_2(\text{g})$ .

T K	$C_p^\circ$	$-(G^\circ - H^\circ(0))/T$	$S^\circ$	$H^\circ - H^\circ(0)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
	$\text{J (mol K)}^{-1}$			$\text{kJ mol}^{-1}$		
0	0.000	0.000	0.000	0.000	-613.278	613.278
25	33.270	144.019	177.264	0.831	-613.789	613.392
50	34.765	167.101	200.582	1.674	-615.134	612.601
75	40.673	180.876	215.650	2.608	-616.716	-610.989
100	49.599	191.203	228.533	3.733	-618.139	-608.858
150	67.975	207.651	252.213	6.684	-620.363	-603.708
200	81.865	221.535	273.793	10.452	-621.935	-597.900
250	91.257	233.958	293.140	14.795	-623.101	-591.756
300	97.552	245.285	310.371	19.526	-624.032	-585.403
350	101.863	255.702	325.753	24.518	-624.872	-578.898
400	104.905	265.337	339.565	29.691	-630.982	-571.862
450	107.120	274.289	352.055	34.995	-631.786	-564.422
500	108.788	282.643	363.432	40.394	-632.479	-556.900
600	111.148	297.824	383.489	51.399	-633.616	-541.672
700	112.832	311.324	400.755	62.602	-634.532	-526.274
800	114.226	323.470	415.915	73.956	-635.297	-510.754
900	115.494	334.506	429.443	85.443	-635.964	-495.145
1000	116.700	344.621	441.674	97.053	-636.575	-479.467
1100	117.855	353.959	452.851	108.781	-637.175	-463.728
1200	118.958	362.635	463.154	120.622	-637.779	-443.009
1300	119.999	370.739	472.717	132.571	-638.395	-410.658
1400	120.974	378.346	481.646	144.620	-638.980	-378.388
1500	121.878	385.515	490.024	156.763	-639.547	-346.200
1600	122.712	392.296	497.916	168.993	-640.096	-314.089
1700	123.477	398.730	505.379	181.303	-640.629	-282.045
1800	124.177	404.853	512.457	193.686	-641.146	-250.074
1900	124.816	410.695	519.188	206.137	-641.648	-218.171
2000	125.398	416.282	525.605	218.648	-642.135	-186.328
2200	126.412	426.773	537.606	243.832	-643.592	-122.811
2400	127.255	436.476	548.643	269.201	-644.994	-59.508
2600	127.959	445.502	558.857	294.724	-646.351	3.609
2800	128.550	453.942	568.362	320.378	-647.666	66.563
3000	129.050	461.869	577.249	346.139	-648.940	129.368
3200	129.473	469.344	585.591	371.992	-650.174	192.043
3400	129.836	476.415	593.452	397.924	-651.378	254.619
3600	130.147	483.126	600.882	423.923	-652.552	317.104
3800	130.417	489.510	607.926	449.980	-653.696	379.515
4000	130.652	495.600	614.622	476.087	-654.810	441.871
4200	130.857	501.421	621.001	502.239	-655.894	504.192
4400	131.037	506.996	627.093	528.428	-656.948	566.476
4600	131.196	512.345	632.921	554.652	-657.972	628.766
4800	131.338	517.486	638.508	580.906	-658.966	691.049
5000	131.464	522.435	643.872	607.186	-659.930	753.356
5200	131.576	527.205	649.031	633.490	-660.864	815.691
5400	131.677	531.810	653.998	659.816	-661.768	878.060
5600	131.769	536.260	658.789	686.161	-662.642	940.488
5800	131.851	540.565	663.414	712.522	-663.486	1,002.987
6000	131.925	544.735	667.885	738.899	-664.300	1,065.546
298.15	97.360	244.883	309.769	19.346	-624.000	-585.641

Uncertainties in Functions					
0	0.000	0.000	0.000	0.000	10.000
298.15	2.000	1.500	2.500	0.300	10.000
1000	3.000	3.000	4.500	1.500	10.000
2000	4.000	4.500	6.500	4.000	11.000
3000	5.000	7.000	9.000	6.000	12.000
4000	6.000	10.000	12.000	8.000	13.000
5000	7.000	13.000	15.000	10.000	14.000
6000	8.000	16.000	18.000	12.000	16.000

hydroxide to the outer surfaces of effusion cells. The most reliable data were obtained by Rao and Schoonmaker [60RAO/SCH]. Even in this phase partial pressures of monomer and dimer can have significant systematic errors, but the ratio of partial pressures seems to be more reliable due to compensation of errors. On this reason, to obtain the value  $\Delta_f H^\circ(\text{Na}_2\text{O}_2\text{H}_2, \text{g})$  we calculated the enthalpy of reaction



The following value of enthalpy for this reaction was found:  $\Delta_f H^\circ(0) = -4.9 \pm 6 \text{ kJ mol}^{-1}$ . The value  $\Delta_f H^\circ(\text{Na}_2\text{O}_2\text{H}_2, \text{g}, 0) = -613 \pm 10 \text{ kJ mol}^{-1}$  corresponds to this enthalpy of reaction.

On the basis of above discussion, we adopt the value

$$\Delta_f H^\circ(\text{Na}_2\text{O}_2\text{H}_2, \text{g}, 298.15 \text{ K}) = -624 \pm 10 \text{ kJ mol}^{-1}.$$

Comparison with the values from other critical reviews is given in Table 3-26.

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### 5. Recommendations for Future Measurements

Having collected and critically reviewed the thermodynamic and spectroscopic data for LiOH, NaOH, and their dimers, there are additional data needed to reduce the uncertainties of the recommended values. We recommend the following measurements:

- (1) the heat capacity of NaOH at low temperatures, especially at  $T < 60$  K.
- (2) the heat capacity and enthalpy increments of crystalline LiOH and NaOH in the region of 50–100 K below the fusion points.
- (3) the heat capacity or enthalpy increments of liquid LiOH and NaOH in the region of 300–500 K above melting points.
- (4) the spectra of LiOH and NaOH under high resolution in gas phase mainly to improve the accuracy of  $\nu_1$  and  $\nu_2$  values.
- (5) the experimental data on structural parameters and vibrational frequencies of  $\text{Li}_2\text{O}_2\text{H}_2$  and  $\text{Na}_2\text{O}_2\text{H}_2$ .
- (6) the  $\text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}$  system by the mass spectrometric method with thorough calibration of the instrument sensitivity using several standards.
- (7) the monomer and dimer partial pressures over LiOH using substantial pressure of water vapor in the effusion cell to prevent decomposition of LiOH.
- (8) the NaOH evaporation by direct mass spectrometric studies to obtain more reliable data on NaOH stability.
- (9) the fragmentation of molecules in vapor over NaOH by mass spectrometric method to clarify the situation with trimer.



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## 5. Recommendations for Future Measurements

Having collected and critically reviewed the thermodynamic and spectroscopic data for LiOH, NaOH, and their dimers, there are additional data needed to reduce the uncertainties of the recommended values. We recommend the following measurements:

- (1) the heat capacity of NaOH at low temperatures, especially at  $T < 60$  K.
- (2) the heat capacity and enthalpy increments of crystalline LiOH and NaOH in the region of 50–100 K below the fusion points.
- (3) the heat capacity or enthalpy increments of liquid LiOH and NaOH in the region of 300–500 K above melting points.
- (4) the spectra of LiOH and NaOH under high resolution in gas phase mainly to improve the accuracy of  $\nu_1$  and  $\nu_2$  values.
- (5) the experimental data on structural parameters and vibrational frequencies of  $\text{Li}_2\text{O}_2\text{H}_2$  and  $\text{Na}_2\text{O}_2\text{H}_2$ .
- (6) the  $\text{Li}_2\text{O}(\text{cr}) + \text{H}_2\text{O}$  system by the mass spectrometric method with thorough calibration of the instrument sensitivity using several standards.
- (7) the monomer and dimer partial pressures over LiOH using substantial pressure of water vapor in the effusion cell to prevent decomposition of LiOH.
- (8) the NaOH evaporation by direct mass spectrometric studies to obtain more reliable data on NaOH stability.
- (9) the fragmentation of molecules in vapor over NaOH by mass spectrometric method to clarify the situation with trimer.