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Mass-spectrometric determination of the thermodynamics of potassium hydroxide and minor potassiumcontaining species required in magnetohydrodynamic power systems^a

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Thermodynamic properties were obtained for several potassium-containing species by means of a series of effusion-mass-spectrometric studies. These included vaporization and dissociation experiments for KOH(g) correlated by both second and third laws, and resulted in a recommended standard enthalpy of formation: $\Delta H_{f}^{2}(298.15 \text{ K}) = -(228.0 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$. MHD electric-power calculations have previously been based on a $\Delta H_{f}^{2}(298.15 \text{ K}) = -(232.6 \pm 12.5) \text{ kJ} \cdot \text{mol}^{-1}$. Of major importance to MHD is the reduction of the uncertainty to $\pm 2 \text{ kJ} \cdot \text{mol}^{-1}$, which reduces the error limits in the computed power from up to 150 per cent to less than 25 per cent. An experimental standard entropy of $(238.1 \pm 4.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was obtained from the second-law correlation for KOH(g). A dissociation energy of $(261.9 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$ for KO(g) to $\text{K}(^2\text{S}_1) \text{ and O}(^3\text{P}_2)$ ground-state atoms was obtained. This study also yielded a value of $(193.3 \pm 16.0) \text{ kJ} \cdot \text{mol}^{-1}$ for $D_0(\text{KH}, \text{g})$ to $\text{K}(^2\text{S}_1)$ and H ground-state atoms, the first reported thermochemical measurement. Second- and third-law calculations of the enthalpy of formation and atomization energy for $\text{K}_2\text{O}(\text{g})$ yielded recommended values of $-(155.5 \pm 12.0) \text{ kJ} \cdot \text{mol}^{-1}$ and $(581.6 \pm 12.0) \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

1. Introduction

Energy requirements for the future might include coal as a promising source for the generation of electric power. In addition to the direct combustion of coal for steam turbines, other methods under consideration are coal gasification and, theoretically, production of electric power using magnetohydrodynamic principles. Small pilot plants employing the magnetohydrodynamic principle have provided a relatively high efficiency of power conversion from the fuel; however, much remains to be done before full-scale success is achievable. One approach being studied is the coal-fired open-cycle MHD power plant involving seeding of the combustion process with small amounts of potassium salts (1 to 1.5 mass per cent). The electric power is derived from the plasma conductivity resulting from the free electrons produced by ionization of the potassium at the high combustion temperature.

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In order to make meaningful computer calculations of the electric conductivity derivable from these systems, a knowledge of the thermodynamic properties of the potassium reactions and their products is required. The combustion of coal in MHD systems involves reaction equilibria of over 200 condensed and gaseous species. Of these, the vapor phase of the compound KOH is of prime importance. As a result of the thermodynamic stability of KOH at the combustion temperature of the MHD system, 2600 to 2800 K, its mole fraction is one to several powers of ten greater than that of either potassium ions or free electrons. For example, a computer calculation of the equilibrium mole fractions of combustion species at 2717 K and 0.6 MPa results in 0.0043 for KOH, 0.0032 for K, 0.00003 for K⁺, and 0.00002 for e⁻.

The current JANAF tables⁽¹⁾ report a ΔH_f° of $-(232.6 \pm 12.5)$ kJ·mol⁻¹ based on a literature survey of the thermochemistry of KOH(g). The uncertainty of ± 12.5 kJ·mol⁻¹ is crucial since it can produce errors of ± 150 per cent in the computed electric conductivity (see figure 1). Therefore, the predicted efficiency, which is so important to the design of large electric power plants, has little meaning.

The remaining K species, including $K_2O(g)$, KO(g), and KH(g), are of minor importance to the electric-conductivity calculations. In addition to these minor species, vapor species involving reactions between K and the inorganic components such as Al and B to form potassium aluminates and borates might reduce the electric conductivity, depending upon the mole fraction of Al and B in the mineral matter of the coal. However, these are also relatively insignificant compared to the mole fraction of KOH(g).

As in other laboratory investigations elsewhere, the present study was undertaken to attempt to reduce the uncertainty in the enthalpy of formation and entropy of KOH(g) to less than $\pm 4 \text{ kJ} \cdot \text{mol}^{-1}$ and $\pm 4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively, and perferably to considerably less. A further objective was to obtain some reasonably definitive experimental bond and atomization energies of the minor K compounds. Both vaporization and dissociation experiments were performed to establish ΔH_f values for KOH(g) based on second- and third-law correlations.



FIGURE 1. Electron mole fraction x_e as a function of the uncertainty in the JANAF-table value of $-(232.6 \pm 12.5) \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta H_f(\text{KOH}, \text{g})$ for the conditions: p = 0.4 MPa and T = 2100 K. For $\Delta H_f(298.15 \text{ K}) = -232.6 \text{ kJ} \cdot \text{mol}^{-1}$, x_e is 17.6×10^{-8} .

1104

2. Experimental

The dual-vacuum-chamber quadrupole mass spectrometer used in these experiments has been described previously.⁽²⁾ The ion intensities were identified by their masses, isotopic distributions, and appearance potentials. The method of determining the mass-spectrometer resolution, as well as the measurement of isotopic-abundance ratios, has been presented previously.⁽³⁾ All quadrupole experimental mass-discrimination effects were taken into account and the necessary corrections to ion-intensity pressure relations were made. Only the chopped, or shutterable, portion of the intensities was recorded, since the mass spectrometer was equipped with a beam modulator and a phase-sensitive amplifier. Ion currents, which originated from species in the molecular beam, appeared as a 30 Hz square wave, while background gases continued to exist as a d.c. current where an a.c. current could be observed in a d.c. signal 1000 times greater.

An alumina effusion cell 25 mm long, with an inside diameter of 6.8 mm, and having an elongated orifice 0.75 mm diameter by 5.5 mm long for beam collimation, was employed. Several reaction systems were utilized. Two experimental procedures were used for the KOH(g) enthalpy and entropy measurements. The first involved the vaporization of KOH(c), while the second was a double-boiler experiment. The KOH(c) (Baker's analyzed) was heated first to a temperature of 723 K, providing a partial pressure of 2.8×10^{-2} Pa. This vapor was then introduced into the effusion cell which was heated to the region of 1200 to 1400 K to dissociate the KOH(g) into K and OH molecules. Temperature measurements to ± 5 K were made by optical pyrometry. The enthalpy results for K₂O(g) were obtained from the dissociation of K₂CO₃.

The experimental procedures for obtaining the enthalpies of formation for KO and KH involved flow reactions of O_2 and H_2 in the effusion cell containing solid K_2O . Since the activity of the solid states is less than unity and solid solutions also occur.⁽⁴⁾ all mass-spectrometer measurements were taken for gas-phase reactions only. This eliminated the necessity to determine the activities of the solids involved.

To obtain the bond energies and the enthalpies of formation it was necessary to ascertain with a high degree of confidence that the measured ion intensities were those from the parent species and not from the fragments of the larger molecules. Therefore, the mass spectrometer was operated at an ionizing potential 1 to 2 V above the appearance potential, which, in nearly all cases, allows only the formation of the ion from the parent species since a fragmentation process usually occurs at higher ionization potentials.⁽⁵⁻⁹⁾ The results for KOH(g), K₂O(g), and KO(g) were obtained from experiments which were conducted in the molecular-flow regime at pressures less than 13 Pa and necessary checks were made to ensure equilibrium within the cell, as described in detail in previously reported studies.^(5,10) However, since the enthalpy of formation of KH(g) is quite positive and is reported to be (123.0 ± 14.6) kJ·mol⁻¹ by Gaydon,⁽¹¹⁾ it was necessary to provide a high mole fraction of H₂ to force the reaction towards KH formation. An H₂ flow resulting in a cell pressure of 1000 Pa was employed. This introduces a flow intermediate between viscous and the free

molecular.⁽¹²⁾ When corrections were applied as given by Dushman,⁽¹²⁾ this introduced a maximum error of $8 \text{ kJ} \cdot \text{mol}^{-1}$ into the ΔH . This error has been included in the total uncertainty for $\Delta H_f(KH)$.

Elemental silver as well as metered O₂ and H₂ pressures were employed for intensity conversion to partial-pressure calibrations. The appearance potentials for the relevant ionic species are listed in table 1. For the reactions, ion-intensities corrections were made for the differences in relative cross-sections and their molecular masses. The relative maximum ionization cross-sections were taken from Mann.⁽¹³⁾ Those for the molecular species were calculated by multiplying the sum of atomic cross-sections by an empirical factor of 0.7.⁽¹⁴⁻¹⁶⁾ These values are probably accurate to ± 30 per cent and for isomolecular reactions would possibly yield errors of $\pm 4 \text{ kJ} \cdot \text{mol}^{-1}$ in the third-law values. Due to the uncertainties in these cross-section estimates, it is advisable to have second-law corroboration for definitive thermodynamic values. Corrections were made for the electron-multiplier gain, which is based on the square root of the molecular mass. Cross-section and multiplier corrections were applied to the individual species intensities, for example $p_i = \{I_i(\sigma\gamma)_{Ag}/I_{Ag}(\sigma\gamma)_i\}p_{Ag}$. Methods of calculation to obtain second- and third-law thermodynamic quantities have been presented in detail previously.^(5,14) The calculated cross-sections σ for the ionic species are given in table 2.

3. Results

ENTHALPY FOR FORMATION AND STANDARD ENTROPY OF KOH(g)

Thermodynamic results were obtained for KOH(g) via vaporization and dissociation experiments. The vaporization reaction:

$$KOH(l) = KOH(g), \tag{1}$$

	<i>I/</i>	V ^u			I/N	7 a	
	This work	Others	Reference		This work	Others	Reference
ĸ	4.5 ± 1.0	4.3	37	K,O	7.5+1.0	7.5 ± 0.1	4
O ₂	12.0 ± 1.0	12.0	37	КН	8.0 ± 1.0	_	
H_2	15.5 ± 1.0	15.4 ± 0.01	37	КОН	7.5 ± 1.0	7.5 <u>±</u> 0.1	27
KO	8.0 ± 1.0	8.0 ± 1.0	4				

TABLE 1. Ionization potentials I

^a Potential employed to accelerate electrons for electron impact ionization.

TABLE 2. Ionization cross-section σ

Species	$\frac{10^{20}\sigma}{m^2}$	Species	$\frac{10^{20}\sigma}{m^2}$	Species	$\frac{10^{20}\sigma}{m^2}$	Species	$\frac{10^{20}\sigma}{m^2}$	Species	$\frac{10^{20}\sigma}{m^2}$	
K	7.67	H ₂	0.33	OH	1.08	КН	5.53	К ₂О	9.77	
H	0.23	O	1.31	O ₂	1.83	КО	6.29	КОН	4.79	

1106

was investigated in the temperature range 700 to 853 K. Ion intensities obtained in this range were converted to partial pressures, and appropriate cross-sections and mass spectrometer corrections were applied, as described in the Experimental section. The equilibrium constants for reaction (1) were calculated from the partial pressures, and are presented in table 3. In the temperature range of the vaporization experiments the mole fraction of the dimer (KOH)₂ was less than 10 per cent and any contribution to the KOH⁺ intensity from fragmentation was negligible.

Values of $\{G^{\circ}(T) - H^{\circ}(298.15 \text{ K})\}/T$ for KOH(l or g) were taken from the JANAF tables.⁽¹⁾ This led to an average third-law vaporization enthalpy of (184.2 ± 0.5) kJ·mol⁻¹. The JANAF tables list a value of $-(424.7\pm0.4)$ kJ·mol⁻¹ for $\Delta H_{\rm f}({\rm KOH}, c, 298.15 \text{ K})$. This is also the recommended value by Wagman et al.⁽¹⁷⁾ The reported $\Delta H_{\rm m}$ in the JANAF tables⁽¹⁾ is (8.62 ± 0.63) kJ·mol⁻¹. They recommended $-(412.7\pm2.0)$ kJ·mol⁻¹ for $\Delta H_{\rm f}({\rm KOH}, 1, 298.15 \text{ K})$ by adding the $\Delta H_{\rm m}$ and the difference between $\{H(679 \text{ K}) - H(298.15 \text{ K})\}$ for the crystal and liquid. Employing this value the results from table 2 yield a third-law value of $-(228.0\pm2.0)$ kJ·mol⁻¹ for $\Delta H_{\rm f}({\rm KOH}, {\rm g}, 298.15 \text{ K})$. The third-law atomization energy of KOH was calculated as 780.7 kJ·mol⁻¹.

The second-law ΔH_{ν} was obtained from a van't Hoff plot of the ion intensities, temperature corrected,⁽¹⁴⁾ as shown in figure 2; ΔH_{ν} at an average temperature of 770 K was calculated as $(170.7 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$. ΔS_{ν} calculated at this temperature is 111.5 J·K⁻¹·mol⁻¹. Employing JANAF thermal functions,⁽¹⁾ a ΔH_{ν} of (185.4±4.0) kJ·mol⁻¹ at 298.15 K was obtained for the liquid vaporizing to the gas. The second-law enthalpy of formation for KOH(g) was calculated as $-(227.2\pm4.0) \text{ kJ} \cdot \text{mol}^{-1}$. The S°(KOH, g, 298.15 K) is $(238.1\pm4.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

To increase the reliability of $\Delta H_f(KOH, g)$ and reduce the uncertainty, the dissociation reaction:

$$KOH(g) = K(g) + OH(g), \qquad (2)$$

was also investigated using a double-boiler experiment in the temperature range 1200 to 1400 K. The KOH vapor was supplied to the effusion cell at a partial pressure of 2.8×10^{-2} Pa. The thermodynamic results for reaction (2) are shown in table 4. Employing JANAF thermal functions,⁽¹⁾ an average third-law $\Delta H(298.15 \text{ K})$ of $(355.6 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ was obtained for dissociation. The listed values for K(g) and OH(g) in the JANAF tables are $(89.2 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ and $(39.0 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$,

TABLE 3. Values of p_{KOH} and $\Delta H(298.15 \text{ K})$ for the reaction: KOH(l) = KOH(g)

Т	Ркон	ΔH(298.15 K)	T	Ркон	ΔH(298.15 K)	T	Ркон	ΔH(298.15 K)
ĸ	Pa	kJ · mol ^{−1}	K	Pa	kJ · mol ^{−1}	ĸ	Pa	kJ·mol ⁻¹
703	1.23×10^{-1}	² 184.5	742	6.36 × 10 ⁻	² 183.8	802	4.84×10^{-1}	184.0
718	2.29×10^{-3}	² 184.5	753	9.54 × 10	² 183.8	824	8.95×10^{-1}	184.3
723	2.79×10^{-3}	² 184.4	774	1.76×10^{-1}	¹ 184.6	833	1.10	184.6
733	4.20×10^{-1}	² 184.3	783	2.64×10^{-1}	¹ 184.0	853	2.06	184.5
							Average	$: 184.2 \pm 0.5$



FIGURE 2. Plots of the logarithm of the partial pressure p against the reciprocal of the temperature; p is an arbitrary pressure.

TABLE 4. Values of p_{KOH} , p_K , p_{OH} , and $\Delta H(298.15 \text{ K})$ for the reaction KOH(g) = K(g) + OH(g)

Т	102 Ркон	103 PK	103 Рон	ΔH(298.15 K)	Т	102 Ркон	$103 p_{\rm K}$	103 ^р он	ΔH(298.15 K)
ĸ	10 ⁻ Pa	$\frac{10^{4}}{Pa}$	$10^{\circ} - \frac{10^{\circ}}{Pa}$	kJ · mol ⁻¹	K	Pa	Pa	Pa	kJ · mol ^{−1}
1200	4.63	0.800	0.761	354.4	1285	4.95	2.47	2.44	355.9
1210	4.66	0.984	0.958	353.1	1293	4.99	2.87	2.67	355.5
1240	4.78	1.28	1.28	356.4	1300	5.01	2.98	2.98	355.9
1253	4.83	1.57	1.58	356.0	1323	5.10	3.91	4.19	355.5
1270	4.90	2.07	1.91	356.0	1343	5.18	4.97	5.32	355.8
1273	4.91	2.16	2.12	355.3	1362	5.25	6.55	6.48	355.5
1275	4.92	2.26	2.22	354.9	1375	5.30	8.14	7.08	355.5
								Average:	355.4 <u>+</u> 2.5

respectively, and are in agreement with those reported by Wagman *et al.*^(17,18) Employing these values of $\Delta H_{f}(KOH, g, 298.15 \text{ K})$ of $-(227.6 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ is calculated, in very close agreement with the vaporization value.

At an average temperature of 1285 K the van't Hoff plot in figure 2 yields $\Delta H_r = (355.6 \pm 6.5) \text{ kJ} \cdot \text{mol}^{-1}$. Reduction to 298.15 K results in $\Delta H_r = (357.4 \pm 6.5) \text{ kJ} \cdot \text{mol}^{-1}$, which yields $-(229.0 \pm 6.5) \text{ kJ} \cdot \text{mol}^{-1}$ for ΔH_f (KOH, g, 298.15 K).

Taking into account the experimental errors and uncertainties in listed thermal functions, the close agreement of the vaporization and dissociation experiments, and

second- and third-law substantiation, recommended values for $\Delta H_f(298.15 \text{ K})$ and S°(KOH, g, 298.15 K) are $-(228.0 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ and $(238.1 \pm 4.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively. The recommended value for the K-OH bond dissociation energy D_0 is $(352.3 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$.

ENTHALPY OF FORMATION OF K₂O(g)

The dissociation of K_2CO_3 yields $K_2O(g)$ and other condensed and vapor species. Since the activity of the condensed phases is less than unity,⁽¹⁹⁾ the $\Delta H_f(K_2O, g)$ was determined from a completely gas-phase reaction:

$$K_2O(g) = 2K(g) + \frac{1}{2}O_2(g),$$
 (3)

in the temperature range 1173 to 1353 K. Values of $\{G^{\circ}(T) - H^{\circ}(298.15 \text{ K})\}/T$ for K(g) and O₂(g) were taken from the JANAF tables;⁽¹⁾ those for K₂O(g) were taken from Ehlert,⁽⁴⁾ who calculated them on the basis of assumed wavenumbers of 300, 50, and 500 cm⁻¹ for the three vibrational modes. The experimental partial pressures shown in table 5 yielded an average $\Delta H(298.15 \text{ K})$ of $(333.6 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ for reaction 3. Employing 89.1 kJ·mol⁻¹ for $\Delta H_f(K, g, 298.15 \text{ K})$, a value of $-(155.5 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ was obtained for the third-law $\Delta H_f(K_2O, g, 298.15 \text{ K})$. A third-law atomization energy of 581.6 kJ·mol⁻¹ was calculated.

The second-law van't Hoff plot for reaction 3 is shown in figure 2. The ΔH of temperature of 1277 K was calculated average as reaction at the (326.3 ± 12.0) kJ·mol⁻¹. Employing an estimated average C_p of 62.8 J·K⁻¹·mol⁻¹ for K₂O(g) between 298 and 1277 K yielded a second-law value of -(152.3+20.0) kJ·mol⁻¹ for $\Delta H_{\rm c}(K_2O, g, 298.15 \text{ K})$. Although there is fairly close agreement between second- and third-law correlations, the third-law value is recommended with an additional uncertainty due to estimating the value of yielding $\Delta H_{\rm f}({\rm K}_{2}{\rm O},{\rm g},298.15~{\rm K})$ $\{G^{\circ}(T) - H^{\circ}(298.15 \text{ K})\}/T$ for $K_{\gamma}O(g),$ $= -(155.5 + 12.0) \text{ kJ} \cdot \text{mol}^{-1}$.

DISSOCIATION ENERGY OF KO(g)

The enthalpy of formation of KO(g) was determined from a study of the reaction of molecular oxygen with the condensed phase of K_2O . The activity and states of the

T	Рк	102 Po,	103 PK.0	ΔH(298.15 K)	Т	<i>p</i> _K	$102 Po_{2}$	103 PK20 4	∆ <i>H</i> (298.15 K)
K	Pa	$\frac{10^{-1}}{Pa}$	Pa	kJ · mol ^{−1}	ĸ	Pa	Pa	Pa	kJ · mol ^{−1}
1173	0.181	4.92	1.56	333.1	1300	0.999	8.18	2.59	334.4
1200	0.266	5.04	1.60	332.7	1305	1.100	8.22	2.60	333.6
1243	0.468	5.22	1.66	333.6	1320	1.410	11.1	3.52	334.0
1263	0.671	7.94	2.52	333.6	1333	1.710	11.2	3.55	332.7
1280	0.701	8.04	2.55	336.0	1353	2.000	11.3	3.60	334.0
								Average:	333.6 ± 2.0

TABLE 5. Values of p_{K} , p_{O_2} , p_{K,O_2} and $\Delta H(298.15 \text{ K})$ for the reaction: $K_2O(g) = 2K(g) + \frac{1}{2}O_2(g)$

 K_2O were not involved since the thermodynamics were obtained from an entirely gasphase study of the decomposition reaction:

$$KO(g) = K(g) + \frac{1}{2}O_2(g).$$
 (4)

The addition of the O₂ helped to force the reaction to favor KO formation.

The experiments were conducted in the 1200 to 1400 K temperature range. Since ΔH of reaction (4) was found to be near zero, second-law calculations were not made. The average $\Delta H(298.15 \text{ K})$ for reaction (4) was 15.9 kJ·mol⁻¹ from the results given in table 6. Employing JANAF thermal functions,⁽¹⁾ $\Delta H_f(KO, g, 298.15 \text{ K}) = (73.1 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$. This yields (261.9 ± 4.0) kJ·mol⁻¹ for the K–O bond energy D_0 , based on dissociation to K(²S₁) and O(³P₂) ground-state atoms.

DISSOCIATION ENERGY OF KH(g)

Similarly to the KO(g) investigation, $\Delta H_f(KH, g)$ was determined in flow reactions of H_2 with the condensed phase of K_2O :

$$KH(g) = K(g) + \frac{1}{2}H_2(g).$$
 (5)

Since K₂O upon decomposition provides a good yield of gaseous K atoms, molecular H₂ was used to react with the K(g) to form KH(g). The results obtained for reaction (5) are presented in table 7. The average $\Delta H(298.15 \text{ K})$ for reaction (5) was $-(21.3\pm0.8) \text{ kJ} \cdot \text{mol}^{-1}$, yielding $(110.0\pm16.0) \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta H_f(\text{KH}, \text{ g}, 298.15 \text{ K})$. The uncertainty of $\pm 16 \text{ kJ} \cdot \text{mol}^{-1}$ includes the possible error of 8 kJ \cdot mol⁻¹ introduced by employing the higher partial pressure of H₂(g). The D₀ for dissociation to ground-state atoms K(²S₁) and H atoms was calculated as $(193.3\pm16.0) \text{ kJ} \cdot \text{mol}^{-1}$.

TABLE 6. Values of p_{K} , p_{O_2} , p_{KO} , and $\Delta H(298.15 \text{ K})$ for the reaction: $KO(g) = K(g) + \frac{1}{2}O_2(g)$

$\frac{T}{K}$	р _к Ра	$10^{-2} \frac{p_{0,}}{Pa}$	<u>рко</u> Ра	$\frac{\Delta H(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	T K	<u>рк</u> Ра	$10^{-2} \frac{p_{O_2}}{Pa}$	<u>рко</u> Ра	$\frac{\Delta H(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$
1283	10.3	3.2	0.142	15.9	1363	17.2	3.4	0.213	15.9

TABLE 7. Values of $p_{\rm K}$, $p_{\rm H_2}$, $p_{\rm KH_2}$ and $\Delta H(298.15 \text{ K})$ for the reaction: $\rm KH(g) = \rm K(g) + \frac{1}{2} \rm H_2(g)$

T	<u>рк</u>	<u>Рн.</u>	<u>Ркн</u>	$\frac{\Delta H(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$
K	Ра	Ра	Ра	
1325	9.24×10^2	2.00×10^{3}	5.7×10^{-1}	- 21.7
1400	7.56 × 10 ²	2.01×10^{2}	5.7×10^{-1}	- 20.9
				Average : -21.3 ± 0.8

4. Discussion

ENTHALPY OF FORMATION AND STANDARD ENTROPY OF KOH(g)

Although the enthalpy of formation of KOH has been under investigation for a number of years by various techniques, including manometry, transpiration, spectroscopic calorimetry, flame spectroscopy, and mass spectroscopy, the measurements were not precise enough for application in current technology. The highlights of these previous experiments are summarized in this section and a comparison is made with the results obtained in our studies.

The vaporization of KOH was first studied by von Wartenberg and Albrech,⁽²⁰⁾ who observed pressures of 33 to 100 kPa from 1443 to 1600 K, with a boiling temperature of 1597 K. In a later transpiration experiment Dubois and Millet⁽²¹⁾ determined a somewhat higher vapor pressure and a boiling temperature of 1540 K. The JANAF tables⁽¹⁾ employed the data of von Warbenberg and Albrech to recommend a value of $(357.3 \pm 12.5) \text{ kJ} \cdot \text{mol}^{-1}$ for $D_0(\text{KOH})$.

Several mass-spectrometer experiments report thermodynamic results for KOH(g);⁽²²⁻²⁷⁾ however, these reported ion species for reaction (1) only, whereas the current study is the first to report ion species for both vaporization (reaction 1) and dissociation (reaction 2). In low-temperature (540 to 725 K) mass-spectrometeric effusion experiments Porter and Schoonmaker⁽²²⁻²⁵⁾ found that mole fractions of the dimer (KOH)₂ were equal to or higher than those of the monomer. Mass-spectrometric studies of both the monomer and dimer were conducted by Gusarov and Gorokhov,⁽²⁶⁾ who reported (354.4±8.0) kJ·mol⁻¹ for $D_0(KOH, g)$. In a later paper⁽²⁷⁾ they reported a new value of (334.7 ± 12.5) kJ·mol⁻¹ for the D_0 and recommended (343.1 ± 12.5) kJ·mol⁻¹ from that obtained in the current study.

An examination of these measurements shows that the dimer $(KOH)_2(g)$ has little or no effect on the mole fraction of K atoms and ions at the temperatures involved in MHD combustion or channel systems. Its mole fraction at a combustion temperature of 2700 K and at low channel temperatures of 2000 K is less than 10^{-6} . Consequently, the assigned error limits of ± 12.5 kJ·mol⁻¹ by the JANAF tables⁽¹⁾ to $\Delta H_f(298.15 \text{ K})$ of $-654.8 \text{ kJ·mol}^{-1}$ for the dimer are considered low enough, requiring no further reduction.

The thermodynamics of KOH have also been studied in high-temperature flames, 1800 to 2500 K, in investigations employing spectroscopic methods of analysis. Jensen and Padley⁽²⁸⁾ reported $(338.9 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$ for $D_0(\text{KOH})$ in flame reactions at 2475 K. Smith and Sugden⁽²⁹⁾ reported $(359.8 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$ by the same method. In cool flames of 1800 K, Cotton and Jenkins⁽³⁰⁾ obtained $(355.6 \pm 8.0) \text{ kJ} \cdot \text{mol}^{-1}$ for $D_0(\text{KOH})$. Gole⁽³¹⁾ in recent spectroscopic chemiluminescence experiments determined a lower bound of 368.2 kJ · mol⁻¹ for D_0 ; however, the status of the molecular and atomic states was not definitively established. Small experimental MHD open-cycle systems have reportedly obtained higher electric power than would be possible if $D_0(\text{KOH}, \text{ g})$ were greater than 368 kJ · mol⁻¹.⁽³²⁻³⁴⁾

In addition to the value of $-(232.6 \pm 12.5) \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta H_f(\text{KOH}, \text{ g}, 298.15 \text{ K})$ recommended by the JANAF tables,⁽¹⁾ the National Bureau of Standards

compilation⁽¹⁷⁾ recommends $-230.9 \text{ kJ} \cdot \text{mol}^{-1}$ with no error limits presented. Their recommended entropy of 238.1 J·K⁻¹·mol⁻¹ is identical to the experimental entropy obtained in this study. Experimental entropies are usually higher than those calculated from spectral quantities by statistical-mechanical methods (the JANAF value is 236.4 J·K⁻¹·mol⁻¹). The calculated values are based on rigid-rotator and harmonic-vibrational models, whereas actual molecules usually have anharmonic effects which contribute slightly to the entropy.

DISSOCIATION ENERGIES OF K₂O(g), KO(g), AND KH(g)

Simmons *et al.*⁽³⁵⁾ decomposed K₂CO₃ at temperatures above 1000 K and observed K₂O(g) as well as K₂CO₃(g), K(g), CO₂(g), and O₂. They reported a second-law ΔH of 321.3 kJ·mol⁻¹ at 1100 K for the decomposition of K₂O(g) via reaction (3). This agrees fairly well with $\Delta H = (326.3 \pm 12.5)$ kJ·mol⁻¹ at 1277 K obtained in the current studies. From other investigations Ehlert⁽⁴⁾ and Byker *et al.*⁽¹⁹⁾ reported $\Delta H_f(K_2O, g, 298.15 \text{ K})$ as $-(142.2 \pm 16.0)$ kJ·mol⁻¹ by assuming a set of frequencies for K₂O and calculating { $G^{\circ}(T) - H^{\circ}(298.15 \text{ K})$ }/T. Our study yielded $-(155.5 \pm 12.0)$ kJ·mol⁻¹.

A value of $(71.1 \pm 42.0) \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta H_f(\text{KO}, \text{ g}, 298.15 \text{ K})$ from bond-energy calculations, and a D_0 of 268 kJ·mol⁻¹ for the bond energy are reported in the JANAF tables.⁽¹⁾ From the decomposition of K₂CO₃ Ehlert⁽⁴⁾ reported (276 ± 12.5) kJ·mol⁻¹ for D_0 . These values are substantially in agreement with the current investigation.

 $D_0(\text{KH}, \text{g})$ has not been previously reported from thermochemical measurements. However, the JANAF tables⁽¹⁾ recommend (123.0±15.0) kJ·mol⁻¹ for $\Delta H_f(298.15 \text{ K})$ from a spectroscopic D_0 of (179.1±15.0) kJ·mol⁻¹ by Herzberg,⁽³⁶⁾ which is approximately 12 kJ·mol⁻¹ less stable than the thermochemical value obtained in this study. Wagman *et al.*⁽¹⁷⁾ recommend 131.4 kJ·mol⁻¹ for $\Delta H_f(\text{KH}, \text{g}, 298.15 \text{ K})$.

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POTASSIUM HYDROXIDE AND OTHER POTASSIUM-CONTAINING SPECIES 1113

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