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# Improvements in the assessment of the thermodynamic properties of condensed and gaseous phases of the CsOH compound



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## ABSTRACT

Thermodynamic properties of condensed and gas phases of the CsOH compound are assessed. Thermal functions of the condensed phase are those already selected in a preceding compilation with some important modification concerning the melting temperature of CsOH(s, γ) that has been re-evaluated to be  $T = 649 \pm 2$  K from recent mass spectrometric determination certifying the total lack of water impurity and from a comparison between the CsOH–H<sub>2</sub>O and the RbOH–H<sub>2</sub>O phase diagram shapes. The vapor phase thermodynamic properties – dealing mainly with the CsOH(g) and Cs<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g) molecules – are re-evaluated from the selection of a new dimerization equilibrium constant and a thorough analysis of preceding vaporization experiments. Besides, flame studies that give directly the dissociation energies of the Cs–OH bond are analyzed from the main assumed reactions as well as considering the different analytical methods as used. The reliability of flame results have also been analyzed in this work by thermodynamic adiabatic calculations of the flame. The mean formation enthalpies as retained in the present analysis are:

$$\Delta_f H^\circ(\text{CsOH, g, 298.15 K}) = -252.7 \pm 7.0 \text{ kJ} \cdot \text{mol}^{-1},$$

and

$$\Delta_f H^\circ(\text{Cs}_2\text{O}_2\text{H}_2, \text{g, 298.15 K}) = -652.0 \pm 11.7 \text{ kJ} \cdot \text{mol}^{-1}.$$

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## 1. Introduction

Caesium is one of the main fission products released in the case of a core meltdown accident of a nuclear reactor. Caesium can rapidly react with a variety of chemical compounds formed as other fission products or structural core materials and then can be transported in the primary cooling system altogether with an important water quantity. As soon as temperature and pressure decrease, the great affinity of Cs(g) for H<sub>2</sub>O(g) as well as the proportions of these components in the material source can lead to an important production of CsOH solid, liquid, or gas in the pipelines of the primary cooling system. In order to predict the intermediate and the final products quantity at the hot break of that pipelines, i.e., in the  $T = (973 \text{ to } 1273)$  K and (1 to 2) bar ranges,

it is important to know accurately the thermodynamic properties of the CsOH condensed and gaseous phases.

About alkaline hydroxides, particularly KOH, RbOH, and CsOH (cr, liq, g), Gurvich *et al.* [1] published in 1997 a large critical review on thermodynamics and molecular properties of the condensed and gaseous phases by comparing the earlier evaluations published in the JANAF tables [2] and in the “Thermodynamic Properties of Individual Substances” of Glushko *et al.* [3,4].

More recent measurements of the Cs<sub>2</sub>O<sub>2</sub>H<sub>2</sub>(g) (dimer) to CsOH(g) (monomer) pressure ratio ( $p_{\text{dim}}/p_{\text{mono}}$ ) by Roki *et al.* [5] showed that it varies from (0.14 to 0.6) within the  $T = (500 \text{ to } 760)$  K contrarily to the 0.2 constant value retained in the above Gurvich *et al.* [1] compilation that leads to a slightly different dimerization enthalpy. Additionally, the melting temperature of CsOH(γ phase) observed by mass spectrometry is higher than the retained one by about  $T = 30$  K and this observation has to be justified more soundly as well as the thermal functions of CsOH (condensed phases) recalculated. The present assessment will

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show how the earlier compilation by Gurvich *et al.* [1] for the CsOH compound can be improved taking into account these new determinations. More, flame studies discarded by Gurvich *et al.* [1] are analyzed from a thermodynamic point of view in order to select the better ways for thermodynamic determinations and to ascertain some of these results.

## 2. Solid and liquid CsOH

### 2.1. Melting temperature of CsOH (solid, $\gamma$ phase)

Gurvich *et al.* [1] retained 8 works according to the criteria of a performed de-hydration step before the experimental determinations that are presented in table 1: these melting temperatures are within the (612 to 619) K range, a scatter been attributed to residual water impurity. If this is really the case, the retained value should be the highest one  $T = 619$  K on the basis of Raoult's cryoscopic law in relation with the unknown final water impurity content since nobody were able to reliably analyze or know this content at the moment of the experimental determinations. Finally, Gurvich *et al.* [1] retained the Konings and Cordfunke [6] DSC value  $T = 615.5$  K – corresponding also to the mean value of the eight determinations – with an uncertainty equal to  $T = \pm 0.5$  K which is in fact the reproducibility of the DSC experiment in place at least of the full range  $T = \pm 4$  K of the selected works.

Recently Roki *et al.* [5] prepared anhydrous CsOH (from monohydrate trade powder grains that are usually the starting material for the samples) by heating this material in its Knudsen cell crucible slowly under vacuum far above the melting and then cooling under vacuum in order to obtain less final reactive surface when opening. Then, the crucible, fitted with its lid and maintained under Ar flow, is transferred in the Knudsen cell and loaded in the mass spectrometer. At the beginning of the mass spectrometric experiment under high vacuum some water vaporized altogether with the CsOH vapor phase ( $H_2O$  partial pressure  $\approx p(CsOH) \cdot 10^{-3}$  in table 4 of Roki *et al.* [5]) as observed in the molecular beam by the mass spectrometer at  $T = 720$  K. During the mass spectrometric

experiments water disappeared from the spectrum and a melting plateau (monovariant system) was observed when temperature decreased at the end of each experiment that corresponds to a true congruent vaporization of pure CsOH. A thermocouple (standard K type thin wires 0.3 mm diam. with small alumina beads 1.2 mm diam.) is located directly under the crucible in a groove and with a long enough path in the Knudsen cell envelope to avoid any thermal leak. This type of device was calibrated according to the main principles as proposed in the IUPAC Knudsen Cell Mass Spectrometric technical report by Drowart *et al.* [14] that lead to an uncertainty in the 0.5 K range as we checked in this laboratory many times at the silver melting temperature. The mean value from five experiments proposed by Roki *et al.* [5] is  $649 \pm 2$  K taking into account the various temperature ramps used for the uncertainty evaluation. This value is far above the preceding determinations as compiled by Gurvich *et al.* [1] which can be explained mainly by the water content since only Roki *et al.* [5] prepared in situ the compound before the melting temperature determination and, thus, certified the lack of water content in the spectrum at a very low level:  $< 1$  ppm by reference to maximum available pressure in the effusion cells means  $< 1$  ppb referred to 1 bar at the melting temperature. Indeed, the preceding studies, probably, were not successful to distillate completely the water content before experiments due to not enough good high vacuum conditions at their treatment temperature, were performed under residual water content in carrier gas flows (1 ppm is a usual limit), by far above the equilibrium adsorption pressure of the pure CsOH(s, or l) at melting, and were needed a transfer between the preparation step and the measurement in different apparatus during which water pollution occurred (as well as reaction with  $CO_2$  from air since carbonates were often analyzed in literature).

Besides, in the compilation of Thermodynamics and Phase Diagrams performed by Sangster [15] on binary salts, we observe that CsOH melted at  $T = 25$  K lower in the binary CsOH–KOH than the retained value from Gurvich *et al.* [1] while the same discrepancies do not exist with RbOH mixtures. As CsOH and RbOH have thermodynamic properties that are similar we can compare their phase diagrams: the  $H_2O$ –CsOH and  $H_2O$ –RbOH systems have been

TABLE 1

Preparation conditions, melting temperatures for CsOH (s,  $\gamma$  phase) from the only authors as retained by Gurvich *et al.* [1], and comparison with the recent value by Roki *et al.* [5] obtained after full water exhaust ascertained by in situ mass spectrometry.

Reference (year)	Method of measurement	Container and conditions	Sample preparation	Melting T/K
Rollet <i>et al.</i> [7] (1963)	Thermal analysis ( $T/\gamma$ )	Closed Ag vessel	CsOH– $H_2O$ dried with $N_2$ flow at $T = 773$ K	619
Cohen-Addad and Ruby [8] (1964)	Thermal analysis ( $T/\gamma$ )		CsOH with $H_2O$ – $Cs_2CO_3$ melted under $N_2$ flow	619
Cohen-Addad and Ruby [9] (1966)	Thermal analysis ( $T/\gamma$ )	Ag vessel	CsOH with $H_2O$ – $CsF$ dried with $N_2$ flow at $T > T_{\text{melting}}$	619
Portnova and Itkina (1974) [10]	DTA under purified Ar or $N_2$ .		CsOH prepared under dry Ar flow – 12 h – at $T = (673 \text{ to } 723)$ K	613
Touzain [11] (1974)	DTA	Ni	CsOH with 2% $Cs_2CO_3$ dried at $T = 573$ K (solid) under vacuum	$613 \pm 4$
Jacobs <i>et al.</i> [12] (1987)	DSC	No information	CsOH–OH + $NH_3$ in autoclave $T = 443$ K, 900 bar	612
Konings and Cordfunke [6] (1990)	Enthalpimetry	Ag spherical ampoule	CsOH $Cs_2CO_3 < 0.02\%$	$597.7 < T_m < 622.8$
Konings <i>et al.</i> [13] (1988)	DSC and preparation	Ag boat	Heated in high vacuum at 700 and then $T = 605$ K	$615.5 \pm 0.5^a$
Roki <i>et al.</i> [5] (2008)	Knudsen cell mass spectrometry (melting plateau at the end of experiments)	Pt-20%Rh cell	CsOH– $H_2O$ first dried under vacuum up to $T = 640$ K then, in situ distillation up to $T = 760$ K in the mass spectrometer when running experiments under high vacuum	647 to 651 ( $\pm 2^a$ )

<sup>a</sup> Reproducibility range.

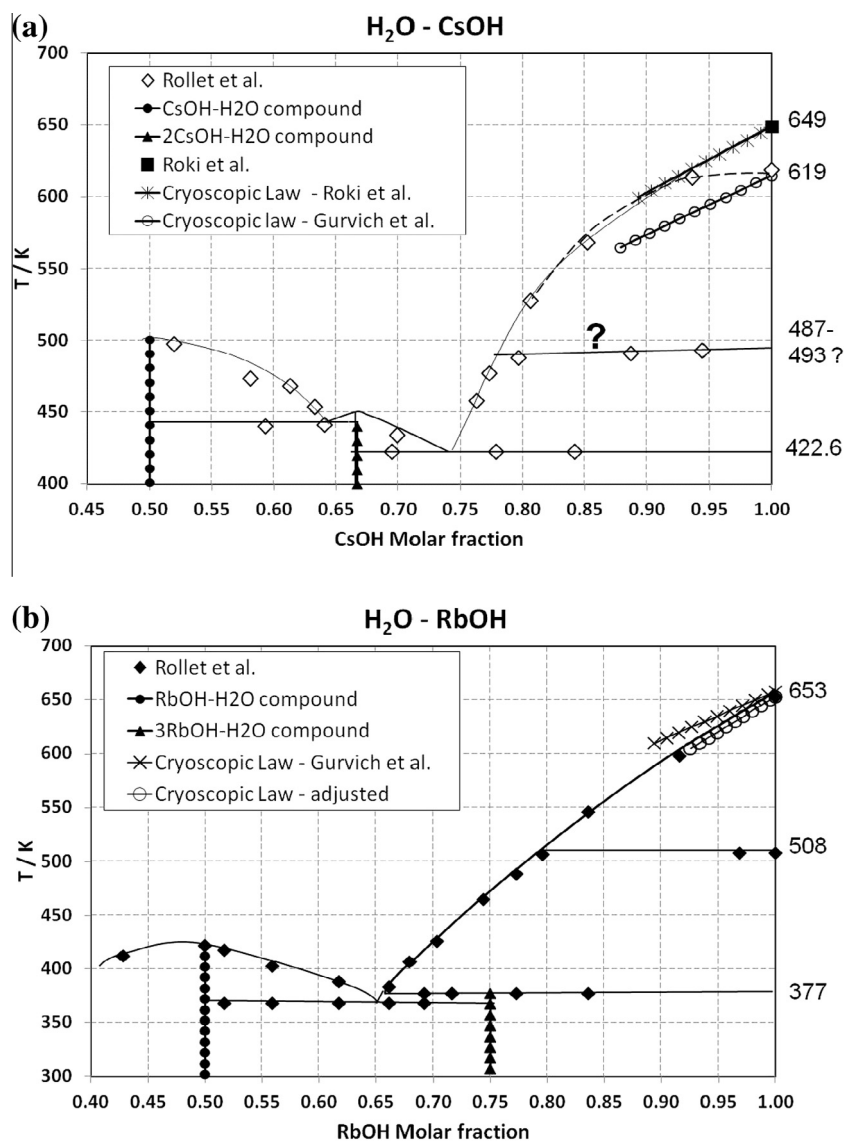
studied by the same team [7,16] using same methods and apparatus. For the H<sub>2</sub>O–CsOH binary system in the original publication the approach of the melting temperature of CsOH as a function of water composition (in mass%) let show a pronounced curvature of the liquidus line close to the melting followed by a quasi-horizontal behavior at the melting. This behavior is also visible in phase diagrams with molar fractions as presented in figure 1a and b. The behavior of the crystallization curve close to the pure compounds CsOH and RbOH should agree with thermodynamics, i.e., the Schröder–van Laar equation (another form for the cryoscopic decrease law) as explained by Prigogine *et al.* [17,18] and according to the relation,

$$-\ln(\gamma_i X_i) = \frac{\Delta_f H}{R} \left( \frac{1}{T} - \frac{1}{T_f} \right) + \frac{C_p^{\circ}(\text{liq}, T_f) - C_p^{\circ}(\text{sol}, T_{\text{fusion}})}{R} \left( \ln \left( \frac{T_f}{T} \right) + 1 - \left( \frac{T_f}{T} \right) \right), \quad (1)$$

in which  $\gamma$ ,  $X$  are, respectively, the activity coefficient and the molar fraction of the compound CsOH or RbOH, and  $f$  is for fusion. This

relation defines rigorously the tangent of the liquidus at the melting of the pure compound but pertains also in the Raoult's law domain for a few percent as presented in figure 1a and b. We observe for the H<sub>2</sub>O–CsOH liquidus a good agreement is obtained with the only melting temperature proposed by Roki *et al.* [5].

For H<sub>2</sub>O–RbOH system the liquidus behavior seems correct meanwhile the only estimated melting enthalpy and heat capacity values by Gurvich *et al.* [1] let appear some small discrepancies: indeed, a melting enthalpy of 5500 J · mol<sup>−1</sup> in place of 8000 – chosen equal to the one for CsOH – optimizes the liquidus shape from the melting temperature proposed by Rollet *et al.* [16], i.e., 654 K. The effect of residual water impurity in CsOH can be also corroborated by the anomalous trend existing for the monovariant solid allotropic transition in CsOH that should be a constant at about  $T = 490$  K as it is for the same transition in RbOH at  $T = 508$  K. The water content in the RbOH compound is in fact easier to distillate than for the CsOH as deduced from observation of other compounds mixed with RbOH and, finally, the liquidus pronounced curvature for CsOH can be attributed reliably to a systematic error in the quoted water content for at least the two last data close to the as mentioned nominal CsOH composition in the Rollet *et al.*



**FIGURE 1.** Comparison of H<sub>2</sub>O–CsOH (a) with H<sub>2</sub>O–RbOH (b) phase diagrams from Rollet *et al.* [7,16] in the vicinity of the pure hydroxide compound with the new melting temperature as proposed by Roki *et al.* [5] for CsOH(s). The Schröder–van Laar relation calculates the tangent at the liquidus for the pure compound (Raoult's cryoscopic decrease law) with the retained thermodynamic data and different melting temperatures.

[7] work. Indeed, the pronounced hygroscopic behavior of CsOH associated to the increasing viscosity of the compound when water content decreases as observed by Ostrovityanova and Itkina [19] in the study of the mixtures (LiOH + CsOH + H<sub>2</sub>O) explains experimental difficulties related to water distillation from CsOH.

## 2.2. Specific heat for CsOH (solid, $\beta$ and $\gamma$ phases)

Gurvich *et al.* [1] selected accurate thermal functions for CsOH(s) at  $T = 298.15$  K from low temperature specific heat measurements taking into account of the  $\alpha \rightarrow \beta$  low temperature transition. At high temperature, from 298.15 K to melting temperature – including the  $\beta \rightarrow \gamma$  transition of CsOH(s) – large discrepancies exist between the direct specific heat determination of Jacobs *et al.* [12] by differential scanning calorimetry (DSC) and the derived values from drop calorimetry enthalpy increments by Konings *et al.* [6] as shown in figure 2. The “anomalous” increase of the heat capacity starting at  $T = 400$  K has been attributed by Konings *et al.* [6] to residual water – that we interpret as a contribution of vaporization enthalpy increasing the measured thermal effect – and this distillation of water seemed to pertain also for the liquid phase just above the melting due to non rigorously closed vessels. This behavior is to be related to the residual water content detected in situ at melting as observed by Roki *et al.* [5] and this water content led to the low and scattered literature values for the melting temperature. As the water vaporization needed a great quantity of heat the total thermal effect when attributed to the only specific heat will result in a serious increase of the measured  $C_p^\circ$ .

As done by Gurvich *et al.* [1] we propose to retain the fits performed by Konings *et al.* [6] for the  $\beta$  and  $\gamma$  phases up to the present proposed melting temperature (649 K) because the residual water content is too low to change drastically the determined calorimetric increment enthalpy values obtained in their closed vessel with no steady-state vaporization losses. Our retained data are presented in table 2. The free energy functions that are useful for the further thermodynamic treatment of the vaporization reactions are also compared in table 2, taking into account either the preceding retained melting temperature by Gurvich *et al.* [1] and Konings *et al.* [6] or with the present proposed value: the difference amounts to  $0.16 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at  $T = 700$  K, i.e., 112 J for the enthalpy of vaporization of the monomer CsOH(g).

As a conclusion, we propose to retain the melting temperature  $T_{\text{fusion}} = 649 \pm 2$  K and the  $C_p^\circ$  values from Konings *et al.* [6] for the

different CsOH condensed phases up to the modified temperature for melting.

## 3. Thermodynamics of the CsOH gaseous phase

In the gaseous CsOH saturated phase the main species are the monomer and dimer molecules since the trimer species exists with a very low partial pressure as observed using mass spectrometry by Roki *et al.* [5], i.e.,  $p(\text{Cs}_3\text{O}_3\text{H}_3, \text{g}) < p(\text{CsOH}, \text{g}) \cdot 10^{-4}$ . Thermal functions of these gaseous species (Free energy function,  $C_p^\circ$ ,  $S_T^\circ$ , and  $H_T^\circ - H_{298.15}^\circ$ ) obtained from their molecular parameters are needed to calculate via second and third laws of thermodynamics the enthalpies of observed reactions.

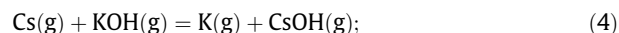
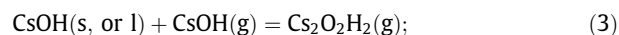
The molecular constants of the monomer and dimer have been recently summarized by Badawi *et al.* [20] in their table 1 and compared to the recent assessment performed by Gurvich *et al.* [1]. The original fully estimated set of molecular parameters reported by Chase *et al.* in JANAF tables [2] (compiled in June 1971) have been clearly improved by Gurvich *et al.* [1] in 1997 taking into account of the further best known CsOH(g) spectroscopic data and of some restricted experimental data set for the dimer by Büchler *et al.* [21], Girichev and Lapshina [22], and Konings *et al.* [23]. A ionic modeling analogous to the one proposed by Belyaeva *et al.* [24] for the KOH(g) dimer ( $D_{2h}$  symmetry) was used in place of the one by Chase *et al.* [2] ( $C_{2h}$  symmetry) to calculate a totally different set of vibration frequencies and, consequently, entropies. The proposed selection for the thermal functions by Gurvich *et al.* [1] are considered reliable within their assigned uncertainties and were used in this work.

In order to obtain the enthalpy of formation of CsOH(g) and  $\text{Cs}_2\text{O}_2\text{H}_2(\text{g})$ , different reactions including these molecules have been studied by different authors that are:

- the dimerization equilibrium:



- the isomolecular equilibria:



- the flame dissociation reaction:

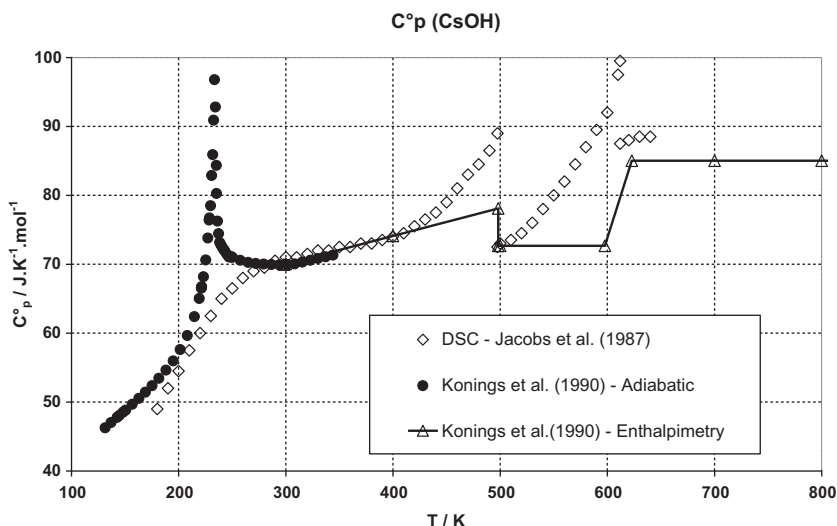


FIGURE 2. Calorimetric determinations of [12] –  $\diamond$ , [6] (table 2) –  $\bullet$  and [6] (table 6) –  $\triangle$  for the CsOH high temperature heat capacity.

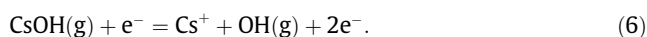


TABLE 2

Thermodynamic data retained in this work for the CsOH condensed phases.

Reference (year)	Retained thermodynamic quantity	Free energy function $-(G^\circ(T) - H^\circ(298.15))/T \cdot \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Gurvich <i>et al.</i> [1] (1997)	$S^\circ(\beta, T = 298.15 \text{ K}) = 104.22 \pm 0.10 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $H^\circ(T = 298.15 \text{ K}) - H^\circ(0 \text{ K}) = 14103 \pm 10 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $T_{\text{trs}}(\beta \rightarrow \gamma) = 498.2 \pm 1.0 \text{ K}$ $\Delta_{\text{trs}} H(\beta \rightarrow \gamma) = 5400 \pm 300 \text{ J} \cdot \text{mol}^{-1}$ $\Delta_{\text{fus}} H(\gamma \rightarrow \text{liq}) = 7780 \pm 4300 \text{ J} \cdot \text{mol}^{-1}$	Fef values quoted in table 56 of Gurvich <i>et al.</i> [1] are totally erroneous. Same for the $C_p^\circ$ relations as proposed in the text.
Konings <i>et al.</i> [6] (1990)	$C_p^\circ(\beta, 298.15 \text{ K}) = 69.96 \pm 0.10 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $C_p^\circ(\beta, T) = 57.8256 + 40.699 \cdot 10^{-3} T$ $C_p^\circ(\gamma, T) = 72.676$ $C_p^\circ(\text{liq}, T) = 85.027$	$= -1.51933\text{E}-07 \cdot T^3 + 3.28373\text{E}-04 \cdot T^2 - 1.46718\text{E}-01 \cdot T + 1.23150\text{E}+02$ (with $T_{\text{fusion}} = 615.5 \text{ K}$ )
This work	$T_{\text{fusion}} = 649 \pm 2 \text{ K}$	$= -1.53281\text{E}-07 \cdot T^3 + 3.30488\text{E}-04 \cdot T^2 - 1.47307\text{E}-01 \cdot T + 1.22831\text{E}+02$

– the dissociative ionization process:



As the dimerization equilibrium constant  $K_d$  obtained from the  $p_{\text{dim}}/p_{\text{mono}}$  experimental ratio value remains an important key value to interpret the vaporization studies and, especially, those of total vapor pressure determinations the new mass spectrometric result by Roki *et al.* [5] engaged us to compare with the original literature vaporization data. The Gurvich *et al.* [1] assessment can be summarized as follow. The  $\text{Cs}_2\text{O}_2\text{H}_2(\text{g})$  to  $\text{CsOH(g)}$  partial pressure mean ratio ( $p_{\text{dim}}/p_{\text{mono}}$ ) had been determined by different authors to vary from 0.7 [25], 0.07 [26–28] to  $\approx 0.001$  [29] at similar mean temperatures since no clear variation was monitored. The latest value has been discarded by Gurvich *et al.* [1] due to “probable mass discrimination effects” in the quadrupole mass analyzer that led to an under-evaluation of the proportion of dimer. The first quoted value was not published by Porter and Schoonmaker [25] because their measurements were performed with hydroxide mixtures and a lower activity than for pure compound leads to a decrease of the present ratio. Due to lack of explanations, we believe that Gurvich *et al.* [1] recalculated this ratio from the Porter and Schoonmaker [25] published heat of dimerization. Gurvich *et al.* [1] chose a ratio  $p_{\text{dim}}/p_{\text{mono}}$  equal to 0.2 which is the geometrical mean of the minimum and maximum values, i.e., 0.07 and 0.7, and this mean value has been assumed to be constant in the range of the mass spectrometric measurements, i.e.,  $T = (570 \text{ to } 770) \text{ K}$ . One third law enthalpy value was deduced for the isomolecular reaction (3) at the  $T = 700 \text{ K}$  arbitrary mean temperature and, then, a dimerization enthalpy is deduced.

Dealing with the Cs–OH bond dissociation studies in flames, Gurvich *et al.* [1] published the dissociation energies issued from flame measurements performing their third-law calculations. However, the flame studies were willingly discarded by Gurvich *et al.* [1] on the basis of probable large associated uncertainties in the knowledge of the free energy functions at so high temperatures where some exited states could not be evaluated. Finally the only conventional vaporization studies were retained for the determination of the monomer standard formation enthalpy.

### 3.1. Conventional thermodynamic studies

Thermodynamic studies on gas phase were performed either using homogeneous gas phase reactions or heterogeneous reactions at equilibrium, i.e., determination of equilibrium pressures over condensed – solid, or liquid – phases. They are done either after analyzing the composition of the vapor phase or from total pressure measurements.

#### 3.1.1. Studies using isomolecular equilibria

Using isomolecular equilibria (3) and (4), Gorokhov *et al.* [27] determined the dissociation energies of  $\text{KOH(g)}$  and  $\text{CsOH(g)}$  by Knudsen cell mass spectrometry (KCMS). Indeed, at the beginning of their experiment, some carbonates impurities produced  $\text{Cs(g)}$  and  $\text{K(g)}$  vapor species in the gas phase due to carbonates decomposition – presumably with  $\text{CO}_2(\text{g})$  production, a molecule that was not quoted to be present in the mass spectrum. The authors attributed the alkaline vapor production to some “unknown reducing conditions” (sic) although the Pt crucible cannot be really considered as imposing any reducing conditions because it is used in mass spectrometry for high oxidant compounds in vaporization studies. It is possible that the measured ions were also related to water pollution, since the ionization process of the hydroxides produces more  $\text{Cs}^+$  (or  $\text{K}^+$ ) fragment ions than  $\text{CsOH}^+$  (or  $\text{KOH}^+$ ) molecular ions, and, finally, the proportions of the  $\text{Cs}^+$  molecular to fragment ions may be difficult to ascertain. To circumvent these difficulties, Gorokhov *et al.* [27] used low electron ionization potentials ( $\approx 6 \text{ V}$ ) close to the ionization potential in order to avoid the production of fragment ions but in this case the assumption of the internal compensation of mass spectrometry sensitivities factors can be in error due to uncertain evolutions of the different ionization cross sections very close to the ionization potential.

Using their obtained equilibrium constant for the isomolecular exchange reaction (4) in the range of  $T = (795 \text{ to } 1044) \text{ K}$ , the  $\text{KOH(g)}$  thermodynamic properties from the Gurvich *et al.* [1] compilation, and the free energy function of JANAF tables [2] for  $\text{Cs(g)}$  and  $\text{K(g)}$ , we obtained the dissociation energy (at  $T = 0 \text{ K}$ ) and the standard formation enthalpy:

$$D_0^\circ(\text{Cs} - \text{OH}) = 375 \pm 12.6 \text{ kJ} \cdot \text{mol}^{-1}, \quad (7)$$

$$\Delta_f H(\text{CsOH, g}, 298.15 \text{ K}) = -263 \pm 12.6 \text{ kJ} \cdot \text{mol}^{-1}. \quad (8)$$

#### 3.1.2. Studies using the dissociative ionization process

For  $\text{CsOH(g)}$  according to the process (6), Gorokhov *et al.* [27] by mass spectrometry obtained the dissociative ionization energy for the  $\text{Cs}^+$  fragment ion threshold appearance as being  $\text{IE}(\text{Cs}^+/\text{CsOH(g)}) + E_{\text{kinetic}} = 7.60 \pm 0.15 \text{ eV}$ .  $E_{\text{kinetic}}$  takes into account the possibility of kinetic energy associated either with the ion or with the neutral species. Using a Born–Haber cycle at  $T = 900 \text{ K}$ , the known adiabatic ionization energy [30] for  $\text{Cs(g)}$ , i.e.,  $\text{IE}(\text{Cs}^+/\text{Cs(g)}) = 3.894 \text{ eV}$  the bond energy value for the reaction  $\text{CsOH(g)} = \text{Cs(g)} + \text{OH(g)}$  has been determined at  $T = 0 \text{ K}$  with the assumption that kinetic energy remains negligible:

$$D_0^\circ(\text{Cs} - \text{OH}) \leq 353.0 \pm 14.8 \text{ kJ} \cdot \text{mol}^{-1}. \quad (9)$$

The inequality  $\leq$  is for the possibility of non negligible kinetic energy. A null kinetic energy contribution was assumed for  $\text{Cs}^+/\text{CsOH(g)}$  by

analogy with the value obtained for  $K^+/\text{KOH}(\text{g})$  already observed by Gorokhov *et al.* [27] using an electrostatic deflection device at the ion source output. But yet this operates for the only kinetic energy associated to measured ions. Our value is slightly different from the Gurvich *et al.* [1] one (i.e.,  $D_0^{\circ}(\text{Cs}-\text{OH}) = 358 \pm 12 \text{ kJ} \cdot \text{mol}^{-1}$ ) because, in the present study the experimental temperature of the molecular beam (and related species) was taken into account in the calculations. The standard formation enthalpy is deduced to be:

$$\Delta_f H^{\circ}(\text{CsOH}, \text{g}, 298.15 \text{ K}) \leq -241.0 \pm 12.1 \text{ kJ} \cdot \text{mol}^{-1}. \quad (10)$$

Using data from Emel'yanov *et al.* [26] (1967) for the ionization thresholds ( $7.46 \pm 0.14 \text{ eV}$ ) from mass spectrometric determinations and the same Born–Haber cycle, we obtained the dissociation energy for  $\text{CsOH}(\text{g})$  and the standard formation enthalpy,

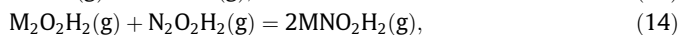
$$D_0^{\circ}(\text{Cs} - \text{OH}) \leq 344.1 \pm 13.5 \text{ kJ} \cdot \text{mol}^{-1}. \quad (11)$$

$$\Delta_f H^{\circ}(\text{CsOH}, \text{g}, 298.15 \text{ K}) \leq -227.6 \pm 13.7 \text{ kJ} \cdot \text{mol}^{-1}. \quad (12)$$

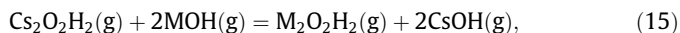
The present large differences in these two above similar studies are due to relative large uncertainties in the fragmentation threshold determination: the proposed accuracy by the authors  $\pm 0.1 \text{ eV}$  ( $11.2 \text{ kJ}$ ) is rarely obtained while the difference in the measurements attained  $0.14 \text{ eV} = 13.5 \text{ kJ}$ .

### 3.1.3. Dimerization enthalpy

Schoonmaker and Porter [25] vaporized by mass spectrometry alkali hydroxides mixtures from condensed phases containing a small quantity of  $\text{CsOH}$  because they could not vaporize pure  $\text{CsOH}$  due to difficulties due to creeping or corrosion problems and associated to the choice of the container material. Monomer and dimer species have been detected in the complex mixed vapors and the ratios of fragment to molecular ions were given at the ionizing energy  $100 \text{ eV}$ . Their ion spectrum for the  $\text{CsOH}$  molecule was very similar to the Roki *et al.* [5] observations for pure  $\text{CsOH}$  vaporization. The considered mixed dimerization reactions were:



with M and N = Na, K, Rb or Cs. For the isomolecular exchange reaction



with M = Rb or K as reference, Schoonmaker and Porter [25] made the assumption that the mass spectrometric sensitivity factors canceled and, consequently, the equilibrium constant  $K_p$  can be written using the only measured ionic intensities as,

$$K_p = [I(\text{M}_2\text{OH}^+) \cdot I(\text{CsOH}^+)^2 / I(\text{Cs}_2\text{OH}^+) \cdot I(\text{MOH}^+)^2]. \quad (16)$$

Using the recommended ionization cross-section values and the secondary electron multiplier yield relations, as proposed in the IUPAC report by Drowart *et al.* [14], and, taking into account the sum of the ionic intensities issued from each molecule (e.g., for the  $\text{CsOH}$  molecule:  $I_{\text{Cs}^+} + I_{\text{CsOH}^+}$ ), we have checked that the authors sensitivity assumption remains available within 9% (i.e., the internal compensation of sensitivity ratio  $\approx 1 \pm 0.09$ ) for the couple  $\text{CsOH}/\text{RbOH}$  and 3% for  $\text{CsOH}/\text{KOH}$  which corresponds to a supplementary uncertainty in the third law enthalpy calculation to be  $0.5$  and  $0.2 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively. If we consider the original thermochemical data obtained by Schoonmaker and Porter [25] from the systems  $\text{RbOH}-\text{CsOH}$  at  $T = 673 \text{ K}$  and  $\text{KOH}-\text{CsOH}$  at  $T = 692 \text{ K}$  (by mass spectrometry) and using the Gurvich *et al.* [1] free energy functions for the reference molecules  $\text{RbOH}(\text{g})$  and  $\text{KOH}(\text{g})$ , we obtain the following dimerization enthalpies for  $\text{CsOH}$ :

with  $\text{RbOH}$  as reference:

$$\Delta_{\text{dimerization}} H^{\circ}(\text{CsOH}, 298.15 \text{ K}) = 146 \pm 11.5 \text{ kJ} \cdot \text{mol}^{-1}, \quad (17)$$

with  $\text{KOH}$  as reference:

$$\Delta_{\text{dimerization}} H^{\circ}(\text{CsOH}, 298.15 \text{ K}) = 156 \pm 10.2 \text{ kJ} \cdot \text{mol}^{-1}. \quad (18)$$

It must be quoted that the dimer  $\text{Rb}_2\text{O}_2\text{H}_2(\text{g})$  cannot be considered *a priori* as a reliable reference since Gurvich *et al.* [1] estimated the bond energy of this molecule due to a lack of direct vaporization studies of  $\text{RbOH}$ . But yet, we observe that the recent value of the third law dimerization enthalpy for  $\text{CsOH}$  at  $T = 298.15 \text{ K}$  obtained by Roki *et al.* [5], i.e.,  $146.6 \pm 7.3 \text{ kJ} \cdot \text{mol}^{-1}$  agrees with the preceding results of Schoonmaker and Porter [25] within the uncertainty limits. For this reason we retained the Roki *et al.* [5] value for further calculations. Note that the difference in the molar fraction of the dimer in the gas phase between Roki *et al.* [5] ( $X_{\text{dimer}} = 0.16$  at  $T = 800 \text{ K}$ ) and Gurvich *et al.* [1] ( $X_{\text{dimer}} = 0.159$  at  $T = 800 \text{ K}$ ) is not significant, meanwhile this mole fraction remains far from the one proposed by Girichev and Lapshina [31] as calculated from electron diffraction data for a molecular beam produced at  $T = 803 \text{ K}$  ( $X_{\text{dimer}} = 0.31 (+0.18, -0.6)$ ). However, the reliability of the dimer mole fraction obtained from electron diffraction may be affected by their estimated total pressure needed for interpretation as well as by a very long flight path ( $0.6 \text{ m}$ ) of these molecules before collection on the photographic plate compared to the mean free path ( $<1 \text{ mm}$ ) at the effusion nozzle that may introduce mass discrimination.

### 3.1.4. Mass spectrometric vaporization studies

Blackburn and Johnson [29] vaporized  $\text{CsOH}$  in a Knudsen cell quadrupole mass spectrometer and calibrated their spectrometer using: – (i) the mass loss of the sample during the experiment, – (ii) the usual estimates for the ionization cross sections ( $\sigma$ ) considering their ratios  $\sigma_{\text{dim}}/\sigma_{\text{mono}} = 2$ , i.e., the “additivity rule”, as proposed further by Drowart *et al.* [14]. Comparison of their data with the earlier mass spectrometric study of Schoonmaker and Porter [25] and with the recent Roki *et al.* [5] determinations shows that their dimer to monomer ionic intensity ratios were by far much lower (i.e., at least 100). The two last teams Schoonmaker and Porter [25] and Roki *et al.* [5] performed their experiments with a conventional magnetic mass analyser which was, in principle, free from mass discriminations as explained by Drowart *et al.* [14]. Thus, as already invoked by Gurvich *et al.* [1], we believe that there is an uncontrolled mass discrimination in the quadrupole mass spectrometer of Blackburn and Johnson [29]. Indeed, these authors attempted to check this mass discrimination “using perfluorotripropylamine for the mass range (50 to 602)” but, finally, they did not retained it for calibration. It can be concluded that Blackburn and Johnson [29] determinations cannot be used for the determination of the dimerization equilibrium constant.

From the Blackburn and Johnson [29] work Gurvich *et al.* [1] re-calculated the dimer contribution from the monomer pressure, but no details were published about the way the correction was obtained. In the present study – as already explained in the preceding recent assessment of the  $\text{CsI}$  compound by Roki *et al.* [32] – applying the Hertz–Knudsen flow relation the apparent total pressure ( $p_{\text{app}}$ ) – was first calculated according to the relation,

$$p_{\text{app}} = p_{\text{mono}} + \sqrt{2}p_{\text{dimer}}, \quad (19)$$

starting from the Blackburn and Johnson [29] published monomer and dimer pressures. A new monomer partial pressure was then re-calculated using these apparent pressure values and the Roki *et al.* [5] equilibrium constant  $K_d$  for the dimerization equilibrium. The published partial pressures given by Blackburn and Johnson (tables 1 and 2 in reference [29]) as presently re-calculated are compared in table 3 and figure 3. Using the present corrected partial

TABLE 3

Re-calculations of the apparent pressure from monomer and dimer pressure values of Blackburn and Johnson [29], the corrected monomer pressure using the dimerization constant  $K_d$  from Roki et al. [5], the calculated third law enthalpy for the only sublimation of the monomer  $\text{CsOH}(\text{cr}) = \text{CsOH}(\text{g})$ .

T/K	Monomer pressure from Blackburn and Johnson [29]/Pa	Dimer pressure from Blackburn and Johnson [29]/Pa	Recalculated apparent pressure/Pa	Monomer pressure corrected with $K_d$ from Roki et al. [5]/Pa	Third law enthalpy $\Delta_{\text{subl}}H^\circ(T = 298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1}$
622	0.056		0.056	0.0381	166.2
654	0.782		0.782	0.364	161.7
672	0.553		0.553	0.356	165.8
681	1.49	0.0394	1.55	0.813	163.1
684	1.68		1.68 1	0.892	163.2
684	1.28		1.28 1	0.739	164.2
686	1.24		1.24	0.738	164.7
702	3.19	0.153	3.41	1.78	162.9
714	3.23		3.23	1.94	164.8
736	5.70		5.70	3.58	165.5
743	8.04	0.181	8.30	4.99	164.8
759	11.6	0.188	11.9	7.41	165.3
772	17.1	0.421	17.7	11.0	165.1
Mean value at $T = 298.15 \text{ K}$					164.4
Standard deviation					1.3

pressures the standard third law sublimation enthalpy at  $T = 298.15 \text{ K}$  is determined:

$$\Delta_{\text{subl}}H^\circ(298.15 \text{ K}) = 164.4 \pm 1.3(\text{standard deviation}) \text{ kJ} \cdot \text{mol}^{-1}. \quad (20)$$

The total uncertainty per experiment is calculated as a combined uncertainty for the standard deviation (defined by Taylor and Kuyatt [33], originally called propagation of errors) and with compensation of errors when taking into account of every steps used in the second and third law enthalpy calculations as explained by Roki et al. [5] in their Appendix B: thus, for the calculation of the final retained total uncertainty we used the minimum value  $\pm 5.3 \text{ kJ} \cdot \text{mol}^{-1}$  which is specific to the present mass spectrometric vaporization experiment added to the standard deviation value (i.e.,  $\pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}$ ). Hence, the final retained total uncertainty is fixed as  $\delta(\Delta_{\text{subl}}H) = \pm 6.6 \text{ kJ} \cdot \text{mol}^{-1}$  and the deduced standard formation enthalpy of  $\text{CsOH}(\text{g})$  becomes

$$\Delta_f H^\circ(\text{CsOH}, \text{g}, 298.15 \text{ K}) = -251.8 \pm 7.1 \text{ kJ} \cdot \text{mol}^{-1}, \quad (21)$$

including the uncertainty of the  $\text{CsOH}(\text{s})$  formation from the Gurvich et al. [1] compilation.

Blackburn and Johnson [29] did not mention any experimental observations concerning the “flow out” from their cell orifice (usually, in Knudsen effusion studies, it is called “creeping” or “surface diffusion along the orifice walls”) as it has been observed for the hydroxides studied by Schoonmaker and Porter [25,34–36] and measured by Roki et al. [5] for the  $\text{CsOH}$  compound. Any such additional flow – on the basis of the flow evaluated by Roki et al. [5] – would increase slightly the present third law enthalpy by  $3 \text{ kJ} \cdot \text{mol}^{-1}$ .

Roki et al. [5], from mass spectrometric vaporization of pure  $\text{CsOH}$ , calculated the third law standard enthalpy for the sublimation to be:

$$\Delta_{\text{subl}}H^\circ(298.15 \text{ K}) = 163.3 \pm 6.5 \text{ kJ} \cdot \text{mol}^{-1}. \quad (22)$$

Using Gurvich et al. [1] standard enthalpy of formation value for the solid  $\text{CsOH}(\text{cr})$  (i.e.,  $\Delta_f H^\circ(\text{CsOH}, \text{cr}, T = 298.15 \text{ K}) = -416.2 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$ ), we calculated the standard enthalpy of formation value for the gaseous  $\text{CsOH}$  as:

$$\Delta_f H^\circ(\text{CsOH}, \text{g}, 298.15 \text{ K}) = -252.9 \pm 7 \text{ kJ} \cdot \text{mol}^{-1}. \quad (23)$$

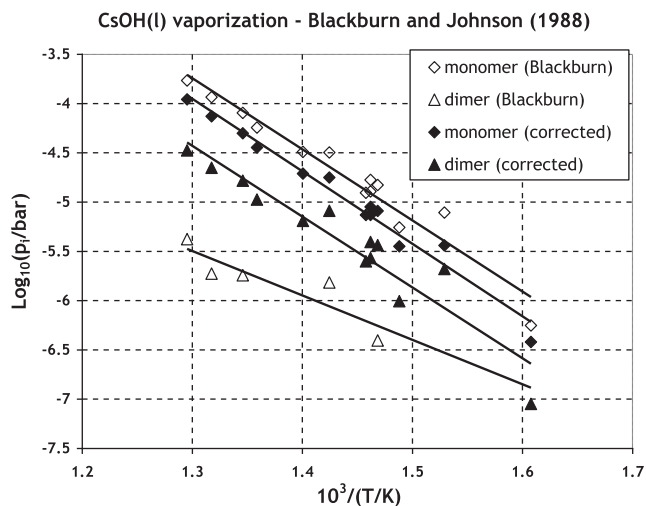


FIGURE 3. Partial pressures in equilibrium with  $\text{CsOH}(\text{l})$  vs. the inverse of temperature from Blackburn and Johnson [29] mass spectrometric data (empty symbols) and re-calculations of these partial pressures from their apparent total pressure using the dimerization enthalpy proposed by Roki et al. [5] (filled symbols) as retained in this work.

### 3.1.5. Total vapor pressure studies

Konings and Cordfunke [28] determined by transpiration method the total Cs atoms transported by an inert gaseous flow within the temperature range (676 to 976) K. For the interpretation, they considered the only monomer assuming that the dimer pressure was negligible. Using our selected dimerization constant ( $K_d$ ) and the apparent pressure in this experiment to be,

$$p_{\text{apparent}} = p_{\text{monomer}} + 2 p_{\text{dimer}}, \quad (24)$$

where  $p_{\text{apparent}}$  value is that published by Cordfunke and Konings [28] from total Cs transported, we re-calculated by the same way as presented by Roki et al. [32] the monomer and dimer partial pressure. As the monomer is considered the main species, third law calculations for the vaporization equilibrium are presented in table 4 with the original pressures [28] and the corrected ones.

These third law results are presented in figure 4 and compared to the Konings and Cordfunke [28] results. Our corrected values are less scattered and they have a smaller trend with measurement temperatures. The total uncertainty was calculated from the third law relationship assuming the combined uncertainties or propagation of errors method [14,33]:



**TABLE 4**

Calculated third law partial enthalpy for the sublimation of the monomer, i.e., the reaction  $\text{CsOH}(\text{cr}) = \text{CsOH}(\text{g})$ , with our selected  $\Delta_f H^\circ$  and with Cordfunke and Konings [28] assumption in their total pressure measurements (lone monomer). The monomer original partial pressure is re-calculated using our selected dissociation enthalpy for the dimer.

T/K	Measured pressure <sup>a</sup> = $p_{\text{app}}/\text{Pa}$ Konings and Cordfunke [28]: their original significant figures	$\Delta H^\circ(T = 298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1}$ Konings and Cordfunke [28] assumption : $p_{\text{mono}} = p_{\text{app}}$	$p_{\text{mono}} = p_{\text{app}} - 2p_{\text{dim}}/\text{Pa}$ our calculation	$\Delta H^\circ(T = 298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1}$ recalculated discarding the dimer
675.7	1.4	158.9	0.713	162.7
686.4	2.42	158.0	1.17	162.1
699.1	5.08	156.2	2.23	161.0
705.6	3.13	160.3	1.74	163.8
737.3	12.22	158.2	6.17	162.4
756.9	21.5	158.2	11.0	162.4
769.4	20.73	160.6	12.1	164.1
781.6	38.34	158.8	20.6	162.8
799.6	67.16	158.0	35.3	162.3
801.3	88.29	156.5	43.1	161.3
804.8	85.09	157.3	43.4	161.8
819.4	124.57	157.0	63.6	161.6
820	106.76	158.2	57.6	162.4
854.6	191.77	159.4	112	163.2
880.5	267.36	160.8	169	164.1
902.6	432.6	160.3	273	163.8
919.4	575.43	160.5	369	163.8
922.2	723.88	159.1	443	162.8
922.3	720.23	159.1	442	162.9
922.4	633.74	160.1	403	163.6
940.8	972.77	159.2	608	162.9
958.1	1199.93	159.8	775	163.3
975.6	1627.13	159.5	1060	163.0
Mean value at $T = 298.15 \text{ K}$		158.9		162.8
Standard deviation		1.3		0.9

<sup>a</sup> The published unit in table 1 of Konings and Cordfunke paper [28] is Pascal and not kPa as mentioned in this table.

$$\delta(\Delta_{\text{subl}} H^\circ) = \left( [\delta T_{\text{mean}} (\Delta_{\text{subl}} H^\circ T_{\text{mean}})]^2 + [(\delta(\Delta_{\text{subl}} \text{Fef}^\circ) T_{\text{mean}})]^2 + \left[ RT_{\text{mean}} \frac{\delta p}{p} \right]^2 \right)^{1/2}$$

$$= \pm 6.5 \text{ kJ} \cdot \text{mol}^{-1}.$$

(25)

In this relation we calculated the total uncertainty for the apparent pressure ( $p_{\text{app}}$ ) taking into account the total monomer pressure uncertainty on the basis of maximum deviation from the original apparent pressure (figure 2 from Konings and Cordfunke [28]) which is  $\delta p_{\text{app}}/p_{\text{app}} = \pm 0.46$  and the uncertainty that amounts for the dimer existence ( $0 < p_{\text{dim}}/p_{\text{mono}} < 0.6$ ) as  $\delta p_{\text{app}}/p_{\text{app}} = \pm 0.3$ .

Hence, the total uncertainty for the apparent pressure was found to be  $\delta p_{\text{app}}/p_{\text{app}} = \pm 0.76$ . For  $T_{\text{mean}} = 800 \text{ K}$  it was considered a temperature uncertainty  $\delta T = \pm 5 \text{ K}$  and  $\delta(\Delta_{\text{subl}} \text{Fef}) = (2 + 2)$  according to Gurvich *et al.* [1] tables. The standard enthalpy of formation was determined,

$$\Delta_f H^\circ(\text{CsOH}, \text{g}, 298.15 \text{ K}) = -253.4 \pm 7 \text{ kJ} \cdot \text{mol}^{-1}, \quad (26)$$

with the total uncertainty including the proposed uncertainty for the stable  $\text{CsOH}(\text{cr})$  standard formation by Gurvich *et al.* [1].

### 3.1.6. Conclusions

As a conclusion for conventional thermodynamic determinations, two main points have to be underlined:

- The recent determination of the dimerization enthalpy by Roki *et al.* [5] agree with earlier values proposed by Schoonmaker and Porter [25]. We retained the Roki *et al.* [5] value which has been obtained after careful examinations of all difficulties encountered to determine the dimer to monomer proportion in the gas phase.
- The third law standard enthalpies of sublimation for the monomer recalculated from pressure values issued from literature data present a better internal consistency with a slightly smaller standard deviation (see tables 3 and 4)

The standard formation enthalpies issued from all vaporization experiments are in better agreement (table 5) than the earlier values proposed by Gurvich *et al.* [1].

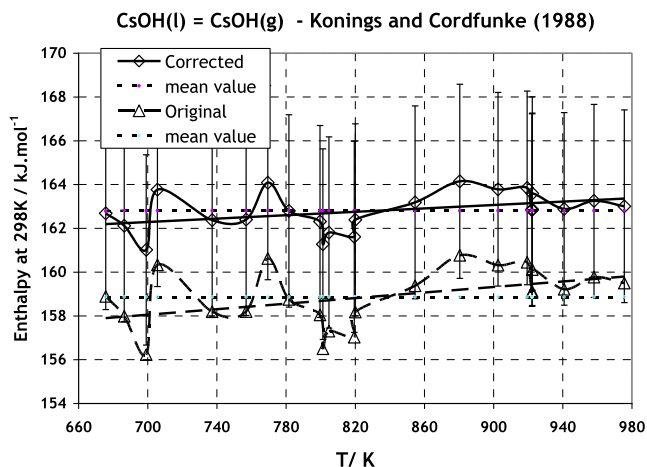
### 3.2. Dissociation energy from flame studies

Most of the measured equilibrium reactions using flame methods were homogeneous gas phase reactions and in the case of  $\text{CsOH}(\text{g})$  measurements were performed by reference to other known species involved in the combustion reaction. In the present work we propose a thermodynamic analysis of these determinations not only in view of determining the best experimental conditions if existing that could lead to retained data but also in view of bracketing future planned kinetic studies based on flames.

In order to obtain the enthalpy of formation of  $\text{CsOH}(\text{g})$ , dissociation enthalpy studies were performed using  $\{\text{H}_2 + \text{O}_2 + \text{N}_2\}$  flames assuming that either the main studied reaction (5) occurred or using a simplified reaction set.  $\text{CsOH}$  was introduced in the flames as a spray of water diluted solution with about 0.1% mol of  $\text{CsOH}$ . The ionization of  $\text{Cs}$  into  $\text{Cs}^+$  liberated electrons at high temperature. The concentration of  $\text{Cs}^+$  (or  $\text{e}^-$ ) was considered small as well as the  $\text{CsOH}(\text{g})$  formed at equilibrium in the above reaction and so the introduced concentration of  $\text{Cs}$  is often chosen as a first approximation for  $\text{Cs}(\text{g})$  residual concentration existing in the flame.

Different detection systems were used: – (i) for electron concentration measurements the method of attenuation of centimetric radio waves, – (ii) for atoms concentration as for instance for  $\text{H}(\text{g})$  concentration the absorption spectroscopy, – (iii) and for  $\text{Cs}(\text{g})$  concentration the double-beam atomic absorption using  $\text{Cs}$  hollow-cathode lamps.

From flame studies the dissociation energy of the  $\text{Cs}-\text{OH}$  bond at  $T = 0 \text{ K}$  was proposed as the main result. Using thermal data of  $\text{CsOH}(\text{s, or g})$  from Gurvich *et al.* [1] and of  $\text{Cs}(\text{g})$  and  $\text{OH}(\text{g})$  from JANAF tables [2], the relation between the flame determined dissociation energy and the formation enthalpy becomes,



**FIGURE 4.** Third law enthalpy of sublimation at 298.15 K vs. the measurements temperature: Konings and Cordfunke [28] original data (triangles) and our data corrected for the dimer contribution to the total apparent pressure (diamonds-shaped).

$$\Delta_f H_{298.15}^\circ(\text{CsOH}, g) = D_0^\circ(\text{Cs} - \text{OH}) + 111.952 \text{ kJ} \cdot \text{mol}^{-1}. \quad (27)$$

The uncertainty is calculated using compensation of errors relation [14] using the published uncertainties in JANAF tables,

$$\delta(\Delta_f H_{298}^\circ(\text{CsOH}, g)) = \left( (\delta(D_0^\circ))^2 + 1.21^2 + 1^2 \right)^{1/2}. \quad (28)$$

It must be quoted that the formation enthalpy of OH(g) from Gurvich *et al.* [1] is slightly different ( $\approx 0.35 \text{ kJ} \cdot \text{mol}^{-1}$ ) than the proposed one in JANAF tables. This difference is included in the usual uncertainties.

**TABLE 5**

Comparison of original literature data from Blackburn and Johnson [29] and from Konings and Cordfunke [28] as recalculated using the 2nd and 3rd law for the sublimation enthalpy of CsOH(g) according to Gurvich *et al.* [1] and the present work.

Reaction : CsOH(cr, l) = CsOH(g)		T range/K	$\Delta_{\text{subl}} H^\circ (T = 298.15 \text{ K, 2nd law}) / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{subl}} H^\circ (T = 298.15 \text{ K, 3rd law}) / \text{kJ} \cdot \text{mol}^{-1}$
Blackburn and Johnson [29]	Reference	622 to 772	$160.9 \pm 9.7^a$	$151.9 \pm 1.9$
	Gurvich <i>et al.</i> [1]		$165.7 \pm 20$	$161.7 \pm 1.1$
	This work		$163.6 \pm 7.0$	$164.4 \pm 1.3^b$
Konings and Cordfunke [28]	Reference	676 to 976	$152.2 \pm 2.6$	$158.9 \pm 1.3$
	Gurvich <i>et al.</i> [1]		$153.8 \pm 8$	$160.2 \pm 0.6$
	This work		$157.9 \pm 1.8$	$162.8 \pm 0.9^b$
Roki <i>et al.</i> [5]		496 to 765	$146.8 \pm 10.1$	$163.3 \pm 2.1^c$

<sup>a</sup> Standard deviations are used as proposed by Drowart *et al.* [14] for intercomparison of pressure determinations.

<sup>b</sup> For 1 experiment.

<sup>c</sup> For 4 experiments.

**TABLE 6**

Formation enthalpies of CsOH(g) at  $T = 298.15 \text{ K}$  as deduced from the original published dissociation energy at  $T = 0 \text{ K}$  in flame studies with our corrected values with new set of evaluated uncertainties. The  $D_0^\circ$  are the measured dissociation energies at  $T = 0 \text{ K}$  for the bond Cs—OH, i.e., the reaction  $\text{CsOH}(g) = \text{Cs}(g) + \text{OH}(g)$ .

Reference (year)	$D_0^\circ$ original / $\text{kJ} \cdot \text{mol}^{-1}$	$D_0^\circ$ corrected / $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H^\circ (T = 298.15 \text{ K}) / \text{kJ} \cdot \text{mol}^{-1}$	Analytical methods
Smith and Sugden (1952) [38]	$387 \pm 12.6$ (2nd law)	$384.3 \pm 12.6$	$-272.4 \pm 20.7^a$	Electron concentration by resonant cavity Same technique and by comparison with LiOH and reference to NaOH full dissociation
Smith and Sugden (1953) [39]	$D_0^\circ(\text{CsOH}) - (\text{LiOH}) 46$ (2nd law)	$D_0^\circ(\text{CsOH}) - (\text{LiOH}) 29.3$ (with present selected entropies)	$-289.2 \pm 15.5^a$	
Jensen and Padley [40] Jensen [41]	$380.7 \pm 12.6$ (3rd law)	$380 \pm 12.6$	$-268.1 \pm 20.7^a$	Electron concentration by resonant cavity Cs absorption H photometry Cs double beam atomic absorption H photometry
Cotton and Jenkins [42]	$376.6 \pm 8.4$ (3rd law)	$376 \pm 8.4$	$-264.1 \pm 8.6$	

<sup>a</sup> This uncertainty takes into account the temperature uncertainty as explained in part 3.2.4. (relation (34)) for very high temperatures in flames.

### 3.2.1. Work of “Smith and Sugden”

Smith and Sugden [37,38] used the Saha equation for ionization equilibrium of CsX salts components in hydrogen/air flames according to the main general reaction,



and with the followed simplified assumptions:  $[\text{Cs}^+]$  concentration was small, Cs(g) concentration in the flame was the one introduced whatever is the  $\text{H}_2/\text{O}_2$  ratio, the CsOH(g) was completely dissociated and the ionization was at equilibrium and, hence,  $[\text{Cs}^+] = [\text{e}^-]$ . For alkali hydroxides, Smith and Sugden [37] observed that – (i) the slope of electron concentration vs. the temperature showed anomalous curvature, – (ii) was not consistent with other salts studies, – (iii) was more pronounced for Rb and Cs hydroxides and – (iv) finally the trend of these slopes did not follow the ionization potentials values as expected for the alkaline series. Different approaches were performed by Smith and Sugden [37] in order to analyze the causes of such behavior, – (i) modification of the burner with an outer nitrogen flow to protect the flame against atmospheric oxygen penetration, – (ii) use of different gas mixtures, – (iii) and taking into account the tendency to form ion pairs and consequently negative ions. Then, Smith and Sugden [37,38] proposed a second and competitive reaction that can explain these discrepancies, i.e., the electron capture by an hydroxyl radical (the electron affinity of OH). This reaction decreased the electron concentration as detected by the method of attenuation of centimetric radio waves. Different experimental conditions were set up, but the authors could not explain the “hook shape” observed for the curves of electron concentration vs. temperature instead of a linear trend. So, Smith and Sugden [38] assumed that a third reaction was occurring simultaneously, i.e., a non negligible residual CsOH(g) concentration remaining in the flame that they called “ion pair recombination” because the formation of CsOH(g) was assumed by the authors to occur in the dead part of the flame from  $\text{Cs}^+$  and  $\text{OH}^-$ .

Because no independent way to determine the hydroxide concentration in the flames existed at that time, Smith and Sugden

[38] estimated *a priori* only for KOH(g) this value using some thermochemical published works in order to check the impact of this third reaction on the theoretical electron concentration curve. From this, they estimated the dissociation energy of the Cs–OH bond by reference to K–OH bond to be 20.9 kJ higher, and they proposed

$$D_0^\circ(\text{Cs} - \text{OH}) = 387 \pm 12.6 \text{ kJ} \cdot \text{mol}^{-1}. \quad (30)$$

The free energy function of CsOH(g) was calculated using estimated molecular parameters at that time by the authors. With the present selected free energy function from Gurvich *et al.* [1], the dissociation energy has to be increased by 7.8 kJ · mol<sup>−1</sup>. As the K–OH dissociation energy currently retained in JANAF tables is smaller by 10.46 kJ, the Smith and Sugden [38] value may be corrected by 7.8 to 10.5 = −2.7 kJ. A summary of original and corrected values is presented in table 6. In the case of CsOH(g) evaluated relatively to KOH(g), the electron affinities of OH varied from (288.7 to 322) kJ · mol<sup>−1</sup> when the proportion of CsOH(g) in the gas varied. This shows how the calculation of the two enthalpies from flame results was not truly reliable.

Finally, to circumvent the difficulties associated to the three main reactions occurring altogether, Smith and Sugden [39] determined directly the Cs–OH dissociation by reference to the Li–OH dissociation. They assumed that these two hydroxides have similar dissociation values and, consequently, the authors presumed quite identical chemical behavior in the flames. The CsOH dissociation energy is thus referred to that of LiOH which was well known (this value is unchanged today). The entropies or free energy functions of CsOH and LiOH must be known for 3rd law calculations of the dissociation energy at  $T = 0$  K. At that time, the molecular parameters for the two molecules, *i.e.*, LiOH(g) and CsOH(g), used in the pre-exponential factor of the equilibrium constant, had been estimated by Smith and Sugden [39]. According to us, using the currently known values – from JANAF tables [2] for LiOH(g) and Gurvich *et al.* [1] for CsOH(g) – the free energy contribution difference in the dissociation energies calculations, *i.e.*, the product  $T\Delta_{\text{diss}}\text{Fef}^\circ_T$  at the flame mean temperature  $T = 2245$  K, is equal to −16.7 kJ · mol<sup>−1</sup> and it must be added to the difference proposed by Smith and Sugden [39]:

$$\begin{aligned} \Delta_r H^\circ_0 &= D_0^\circ(\text{Li} - \text{OH}) - D_0^\circ(\text{Cs} - \text{OH}) = 46.0 - 16.7 \\ &= 29.3 \text{ kJ} \cdot \text{mol}^{-1}. \end{aligned} \quad (31)$$

From JANAF tables [2] the dissociation energy for LiOH is  $D_0^\circ(\text{Li} - \text{OH}) = 430.4 \pm 6.5 \text{ kJ} \cdot \text{mol}^{-1}$  and consequently for CsOH the calculated value is  $D_0^\circ(\text{Cs} - \text{OH}) = 401.1 \pm 7.5 \text{ kJ} \cdot \text{mol}^{-1}$ . The original and the corrected dissociation energies as well as the formation enthalpy of CsOH(g) are presented in table 6.

### 3.2.2. Work of “Jensen and Padley”

Jensen and Padley [40] and Jensen [41] studied mainly the reaction (5) with the Cs concentration balance written as,

$$[\text{Cs}^\circ] = [\text{Cs}, \text{g}] + [\text{CsOH}, \text{g}] + [\text{e}^-]. \quad (32)$$

The electron concentration – assumed to be equal to the  $[\text{Cs}^+]$  concentration by ionization at equilibrium – was determined using a special calibration procedure. In the flames within the temperature range (2000 to 2500) K the linear response obtained by the authors [40,41] can be regarded as if there is no OH<sup>−</sup> competitive formation because they never spoke about this possibility. The alkaline gas concentration  $[\text{Cs}, \text{g}]$  was determined by optical absorption measurements using the first resonant doublets of the alkaline component (with the highest level populated at the flame temperature and 1 atmosphere pressure) and the H concentration by usual photometry. In order to produce a relative proportion of positive ions and, hence, electron concentrations clearly measurable, the authors

introduced some additional salt in the flame – the so-called suppressed-ionization technique. In the case of CsOH the addition of Rb salt (the nature of the salt as RbCl or RbOH is not mentioned) they could not “suppress” sufficiently the ionization of Cs. Consequently, the linear range in the graph representing the ion concentration  $[\text{Cs}^+]$  vs. temperature (not presented for Cs in their publication) was probably very small and, in any case, limited by the highest concentrations of Cs that can be introduced in the vaporizer. With such conditions in relation (30) the CsOH(g) concentration should remain small compared to other species.

Their proposed dissociation energy value  $D_0^\circ$  at  $T = 0$  K is equal to  $380.7 \pm 12.6 \text{ kJ} \cdot \text{mol}^{-1}$ . Further, it was corrected by Jensen [41] taking into account the linear Cs–O–H structure and becomes  $380 \pm 12.6 \text{ kJ} \cdot \text{mol}^{-1}$  as presented in table 6. Note that the linear structure of the CsOH molecule as well as its molecular parameters agree with the present retained selection by Gurvich *et al.* [1]

### 3.2.3. Work of “Cotton and Jenkins”

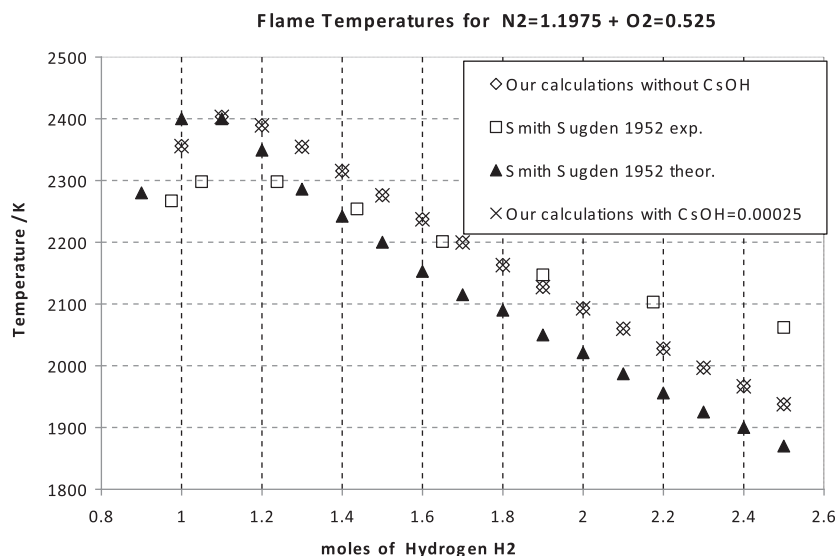
Cotton and Jenkins [42,43] considered in their work on alkaline earth metal that the main reaction was the equilibrium (5). The ion and electron concentrations were not measured in order to avoid any error due to an erroneous electrical balance with unidentified ions, and they used low flame temperature (1570 K) in order to neglect the ionization into  $\text{Cs}^+$  in the Cs balance. They measured  $[\text{Cs}, \text{g}]$  concentration by atomic absorption (Cs lamps) using a double-beam for calibration. In the post reaction zone of the flame, the measurement of  $1/[\text{Cs}]$  as a function of  $1/[\text{H}]$  led to the evaluation of the equilibrium constant  $K_p$  using the slope of the curve. The conditions for measurements were:

- The  $[\text{H}]$  concentration in the post reaction zone was measured by the Li/LiOH absorption method (set up in a LiOH flame) and remained higher than expected at equilibrium – it was a well known feature for the present H “radicals” –,
- Despite this non-equilibrium feature, the above reaction (5) was assumed to occur according to equilibrium ( $K_p$  value remains the one at equilibrium) and so the  $\text{Cs}(\text{g})$  concentration increased detrimental to CsOH(g),
- The water concentration  $[\text{H}_2\text{O}]$  in the flame was the same as introduced due to saturation effect,
- The hydrogen flow rate variations were limited to a maximum temperature variation of the flame equal to 20 K.

A mean value at  $T = 1570$  K is obtained for the equilibrium constant  $K_p$ . Entropies and free energy functions for CsOH(g) are those from Jensen and Padley [40], and, consequently, the correction to be applied is  $\approx -(0.4 \text{ to } 0.7) \text{ kJ}$ . The uncertainty on the dissociation energy determination was dependent on the Li/LiOH absorption method used to determine the H concentration. The authors said that some errors compensation occurred. Formation enthalpies of CsOH(g) at  $T = 298.15$  K as deduced from flame studies and corrected values are presented in table 6.

### 3.2.4. Uncertainty of flame temperature

For many flame studies at that time, the temperature of the flame was deduced from the sodium D-line reversal method previously tested in independent experiments of temperature calibration of the burners. Sometimes also small quantities of sodium were added to the flame in the studies of different salts. Greig [44] analyzed the intrinsic physico-chemical difficulties in those measurements, at least those coming from the state of equilibrium of the different components of the flame – molecules, atoms (*i.e.*, related to the gas temperature) electrons and ions (plasma temperature) – each of these components having their own temperatures. Best conditions were those existing in the dead area of the flames where the electron concentration was low and the Na atomic elec-



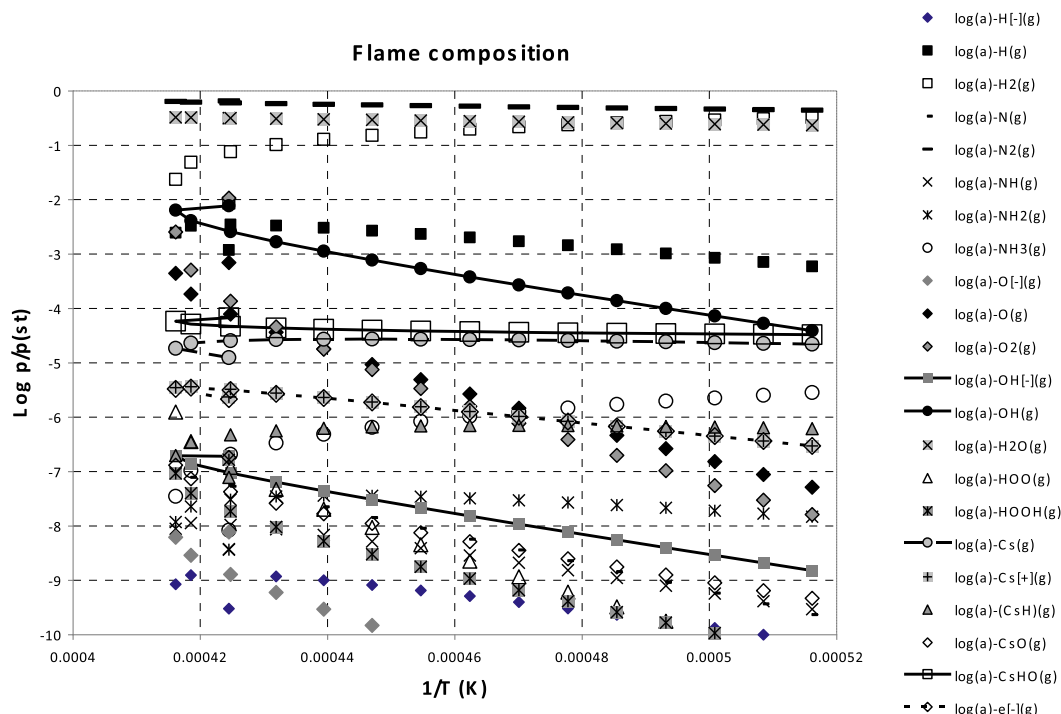
**FIGURE 5.** Comparison of experimental (via reversal sodium D-line) and calculated by Smith and Sugden [38] flame temperatures and adiabatic calculations from this work. Flame inputs are those from Smith and Sugden [38].

tron population stabilized in a steady-state. These conditions were those occurring in the preceding analyzed works only for limited  $\text{Cs}^+$  (or  $\text{e}^-$ ) concentrations. Indeed method based on the electron concentration may present some unusual trends when this concentration becomes too important. Greig [44] proposed a temperature uncertainty equal to 1% in the (1000 to 4000) K range (10 to 40 K).

Independently of the sodium D-line reversal method to determine the temperature as well as complementary pyrometric works, the flame temperature can be calculated by thermodynamics under adiabatic conditions. Smith and Sugden [38] compared the so-calculated temperatures with the experimental ones. Data

are presented in figure 5 altogether with our calculated flame temperatures corresponding to the same conditions.

In the original Smith and Sugden [38] data set, large differences exist between experimental and theoretical temperatures (100 to 200 K) and, moreover, the sign of the difference changes at about 2300 K where the two curves cross. Smith and Sugden [38] explained the difference at low temperature by the indrawn air in the flame, i.e., excess of oxygen introduced in the flame that burned and, consequently, increased the flame temperature. In the high temperature range the flame may not be adiabatic due to heat losses by radiation or convection exchanges, and the measured temperature became lower than the calculated one.



**FIGURE 6.** Present thermodynamic adiabatic calculation of the activity of the *i*-species in the Smith and Sugden [38] flame input composition including atoms, molecules, ions and electrons.

**TABLE 7**

Set of gaseous and ionic species taken into account in the thermodynamic calculations of the adiabatic thermal equilibrium of the flame.

Nature of species	Species from SGTE data bank except for CsOH(g), Cs <sub>2</sub> O <sub>2</sub> H <sub>2</sub> (g) as selected in this work
Atomic gases	H, O, N, Cs
Gaseous molecules	O <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> , N <sub>3</sub> , H <sub>2</sub> , OH, H <sub>2</sub> O, HO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> , NH, NH <sub>2</sub> , NH <sub>3</sub> , N <sub>2</sub> H <sub>2</sub> , N <sub>2</sub> H <sub>4</sub> , CsOH, Cs <sub>2</sub> O <sub>2</sub> H <sub>2</sub> , CsO, Cs <sub>2</sub> O, Cs <sub>2</sub> O <sub>2</sub> , Cs <sub>2</sub> , CsH
Gaseous ions	O <sup>-</sup> , H <sup>-</sup> , H <sub>2</sub> <sup>-</sup> , OH <sup>-</sup> , N <sup>-</sup> , e <sup>-</sup> , N <sub>2</sub> <sup>-</sup> , Cs <sup>-</sup> , Cs <sup>+</sup> , O <sup>+</sup> , H <sup>+</sup> , H <sub>2</sub> <sup>+</sup> , OH <sup>+</sup> , Cs <sub>2</sub> O <sup>+</sup> , CsOH <sup>+</sup> , N <sup>+</sup> , N <sub>2</sub> <sup>+</sup> , H <sub>3</sub> O <sup>+</sup>

Our calculations disagree with those of Smith and Sugden [38] – probably due to more recent and accurate data or available calculation methods – and are in better agreement with experimental data. The remaining difference with experimental data may come also from the non equilibrium state of some components in the flame, for instance the excess of H coming from non reacted species as measured by Cotton and Jenkins [42] that rendered the thermodynamic enthalpy balance not exact (the H recombination is exothermic). This is depending on the H concentration related to equilibrium. Besides we observed in our calculations that the small quantity of CsOH introduced does not change the adiabatic temperature of the flame.

Temperature gradients were an additional source of uncertainty. They have been measured by Smith and Sugden [37] and they were reduced when using N<sub>2</sub> sheathed flames in order to obtain more uniform temperatures. In their analysis, Smith and Sugden [38] showed that for sheathed flames at their centre (which is around 5 mm large for a 1 cm flame width) the temperature gradient varies from 10 K for air rich to 60 K for H<sub>2</sub> rich flames respectively.

According to us, the uncertainty in the temperature to characterize the gaseous reactions studied in flames is particularly difficult to be estimated. One part of the uncertainty is coming from the physical and chemical phenomena as discussed by Greig [44], i.e.,  $T = (10 \text{ to } 40) \text{ K}$ , and another part of the uncertainty is coming from the matter heat exchange between the flame and the surrounding atmosphere that generates temperature gradients from (10 to 60) K. Consequently, we believe that the total uncertainty

amounts at least to  $\pm 50 \text{ K}$  varying with temperature, and, thus, any calculations of thermodynamic properties based on second law (slope of  $K_p$  or a related value as a function of temperature) must be discarded unless the only mid value is used for direct measurements of the equilibrium constant. In case of third law calculations, the impact of the uncertainty on temperature is less pronounced as already explained by Drowart *et al.* [14] for thermodynamic calculations from gas phase determinations. In the present case for the dissociation reaction, with a  $T = 50 \text{ K}$  uncertainty, is:

$$\delta_{\text{diss}} H_{2400 \text{ K}}^{\circ} = (-R \ln K_p(2400 \text{ K}) + \Delta F_{2400 \text{ K}}^{\circ}) \cdot \delta T = 8.0 \text{ kJ}. \quad (33)$$

This uncertainty has to be added to the proposed one in flame studies at high temperature.

### 3.2.5. Flame composition

In order to evaluate the flame composition, thermodynamic calculations under adiabatic conditions for the flame as set up by Smith and Sugden [38] were performed and are presented in figure 6, limited to the 0.1 ppb range and within the  $T = (1930 \text{ to } 2360) \text{ K}$  range. Thermodynamic data used are those from Gurvich *et al.* [1] in which we added the present selection for CsOH gas phase as performed in this work. The whole set of gaseous and ionic species taken into account in the calculations is presented in table 7.

In figure 6, it can be seen that the  $[\text{OH}^-]$  concentration was always observed lower than  $[\text{Cs}^+]$  concentration by a factor varying from 100 at  $T = 1930 \text{ K}$  to 10 at  $T = 2360 \text{ K}$ .

**TABLE 8**Summary of all determined and presently corrected values for the dissociation enthalpy of Cs–OH at  $T = 0 \text{ K}$  and the resulting standard formation enthalpy of CsOH(g) at  $T = 298.15 \text{ K}$ , quoted with total estimated uncertainties.

Reference (year)	Experimental methods and studied reactions	$\Delta_f H^{\circ}(\text{CsOH(g)}, T = 298.15 \text{ K}) / \text{kJ} \cdot \text{mol}^{-1}$	Comments
Smith, Sugden (1952) [38]	Flames $\text{Cs(g)} + \text{H}_2\text{O(g)} = \text{CsOH(g)} + \text{H(g)}$	$-272.4 \pm 20.7$	Possible excited states large temperature uncertainty other reactions occurring
Smith and Sugden (1953) [39]	Flames/reference $\text{LiOH Cs(g)} + \text{H}_2\text{O(g)} = \text{CsOH(g)} + \text{H(g)}$	$-289.2 \pm 15.5$	Possible excited states large temperature uncertainty
Jensen and Padley (1966) [40,41]	Flames $\text{Cs(g)} + \text{H}_2\text{O(g)} = \text{CsOH(g)} + \text{H(g)}$	$-268.1 \pm 20.7$	
Cotton and Jenkins (1969) [42]	Flames $\text{Cs(g)} + \text{H}_2\text{O(g)} = \text{CsOH(g)} + \text{H(g)}$	$-264.1 \pm 8.6$	Low flame temperature
Schoonmaker and Porter (1959) [25]	HTMS isomolecular reaction $\text{M} = \text{K}$ or $\text{Rb} (\text{CsOH})_2(\text{g}) + 2 \text{ MOH (g)} = (\text{MOH})_2(\text{g}) + 2 \text{ CsOH(g)}$		First determination of dimerization constant
Gorokhov <i>et al.</i> (1970) [27]	HTMS–Dissociative ionization $\text{CsOH(g)} = \text{Cs}^+ + \text{OH(g)} + \text{e}^-$	$\leq -241.0 \pm 14.9^a$	Possible kinetic energy and large uncertainty from electron energies
Emel'yanov <i>et al.</i> (1967) [26]	HTMS–dissociative ionization $\text{CsOH(g)} = \text{Cs}^+ + \text{OH(g)} + \text{e}^-$	$\leq -227.6 \pm 12.1^a$	
Gorokhov <i>et al.</i> (1970) [27]	HTMS–isomolecular reaction $\text{Cs(g)} + \text{KOH(g)} = \text{K(g)} + \text{CsOH(g)}$	$-263.0 \pm 12.6^b$	Possible different origins for Cs(g) and K(g)?
Blackburn and Johnson (1988) [29]	HTMS–vaporization $\text{CsOH(l)} = \text{CsOH(g)}$	$-251.8 \pm 7.1^b$	Corrected with Roki <i>et al.</i> [5] dimerization constant
Konings and Cordfunke (1988) [28]	Transpiration–vaporization $\text{CsOH(l)} = \text{CsOH(g)}$	$-253.4 \pm 7^b$	
Roki <i>et al.</i> (2007) [5]	HTMS–vaporization $\text{CsOH(l)} = \text{CsOH(g)}$	$-252.9 \pm 7^b$	New determination of dimerization constant
Gurvich <i>et al.</i> [1] (1997)	Preceding assessment	$-256.0 \pm 5^a$	Vaporization reactions are retained
This work	Our assessment including new determinations	$-252.7 \pm 7.0^c$	Retained value

<sup>a</sup> Original uncertainties proposed by the authors.<sup>b</sup> Uncertainties re-evaluated in this work.<sup>c</sup> Evaluated as  $[\sqrt{(7.1^2 + 7^2 + 7^2)/n}]$  (with  $n = 3$ ) means compensation of errors.



Consequently, the electron  $[e^-]$  and  $[Cs^+]$  concentrations were quite equal in the absence of any other significant ion concentration ( $H^-$  for instance) especially at  $T < 2000$  K.

The gaseous hydroxide  $CsOH(g)$  appears to be non totally decomposed: at low temperature, its concentration is quite equal to the concentration of  $OH(g)$ , meanwhile for the high temperature range, as the  $OH(g)$  concentration increases (coming from water vapor) the simultaneous increase of the  $CsOH(g)$  concentration imposes a decrease of the  $Cs(g)$  concentration. Consequently, the  $[Cs^+]$  concentration decreases. The shape of the concentration curves explains also the “hook shape” observed in the electron concentration curves as monitored from flames studies by Smith and Sugden [38]. According to us, when using the resonant cavity method, the Saha equation could not be used as long as the  $CsOH(g)$  molecule remains not totally or not enough decomposed. This was particularly the case for the  $CsOH$  flame studies by Smith and Sugden [37,38].

### 3.2.6. Conclusions on flames

As a conclusion for flame studies, it can be retained that:

- the main selected reaction set were not always the most significant one used for results interpretation,
- in particular case of  $CsOH(g)$ , the decomposition was not total and it had to be evaluated by an independent way,
- the excited states were not always identified or taken into account when existing,
- the equilibrium conditions were difficult to ascertain since the only observed evolution in the flame when going towards the output (dead zone) did not warranty sufficient long time to achieve the attainment of fundamental electronic levels for the reactants and for the products. Other species as for example  $H(g)$  modifies the equilibrium conditions due to kinetic limitations for its recombination into  $H_2(g)$ .

Gurvich *et al.* [1] invoked also a significant uncertainty on third law analysis due to the high temperatures used in flames, *i.e.*, 2475 K for Jensen and Padley [40], and consequences on thermal function uncertainties but this was not so significant for Cotton and Jenkins [42] who worked at rather low temperatures

$\approx 1570$  K. For the above analyzed and presently quoted reasons, we believe that very high temperature flames studies of  $CsOH(g)$  –  $\approx 2475$  K – cannot be retained. Among the present flame studies and after the present thermodynamic analysis, the only work of Cotton and Jenkins [42] performed at lower temperatures seems reliable and can be compared to conventional thermochemical results.

## 4. Conclusions and retained data

Retained thermodynamic data for the solid and liquid phases have been presented in table 2. For the gaseous phase the whole set of formation enthalpies from different studied reactions using assessed thermal functions from Gurvich *et al.* [1] for  $CsOH(g)$  and JANAF tables [2] for other reference compounds is summarized in table 8. Figure 7 illustrates the overlaps from the present evaluation taking into account of the total uncertainties.

Born–Haber cycles based on dissociative ionization as observed in mass spectrometry [26,27] were never accurate enough nor reliable due to the existence of a possible excess kinetic energy associated to the dissociative ionization process that was not detected. The isomolecular [27] type reaction (5), taking into account  $Cs(g)$  and  $K(g)$ , in addition to the hydroxides ( $CsOH$  and  $KOH$ ) in the gas phase, was based on chemical reducing conditions due to pollution by an oxide or a carbonate as invoked by Gorokhov *et al.* [27]. The fact that the results were far from the vaporization ones – but nevertheless in agreement within the uncertainty range – let suppose that the internal compensation of mass spectrometric sensitivities was not working accurately.

Good agreement is observed for the three values obtained by direct sublimation, confirming within their uncertainty limits the choice of these retained original data by Gurvich *et al.* [1]. We retain also a mean value from sublimation experiments when adding the last value from Roki *et al.* [5]. The proposed mean value for the formation enthalpy of  $CsOH(g)$  is,

$$\Delta_f H^\circ (CsOH, g, 298.15 \text{ K}) = -252.7 \pm 7.0 \text{ kJ} \cdot \text{mol}^{-1}. \quad (34)$$

The present retained value is slightly different from that proposed by Gurvich *et al.* [1], *i.e.*,  $(-256.0 \pm 5 \text{ kJ} \cdot \text{mol}^{-1})$ . The difference in the resulting monomer pressure can be calculated using the third law relation,

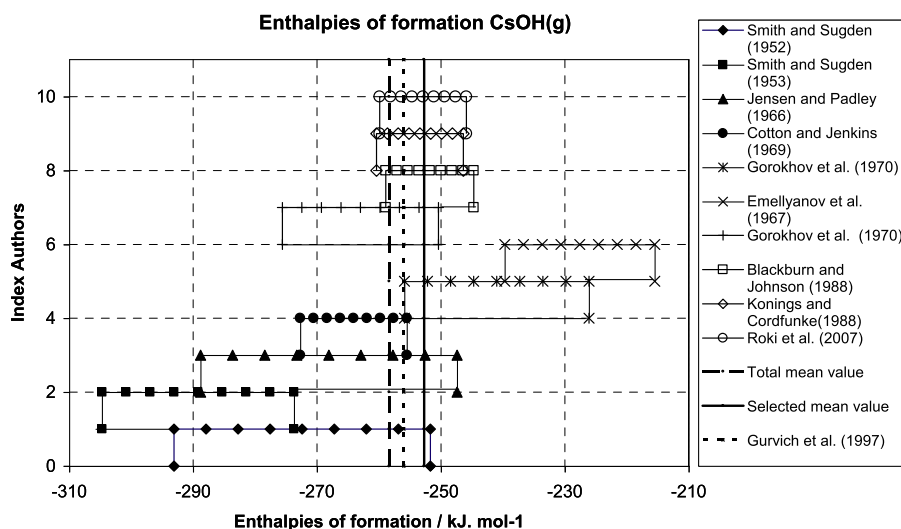


FIGURE 7. Summary of all determinations of the standard formation enthalpy of  $CsOH(g)$  at  $T = 298.15$  K including the uncertainty ranges and comparison between the early retained value from Gurvich *et al.* [1], the total mean value and our retained value.

$$\frac{\partial p}{p} = \frac{\partial \Delta_f H}{RT} + \frac{\partial \Delta_f G}{R} = 3000/RT, \quad (35)$$

using the retained  $G_f$  from Gurvich *et al.* [1]. At  $T = 1000$  K – the temperature of the cold point of the hot branch of the nuclear plant primary line – the monomer pressure is lower by 36% than from Gurvich *et al.* [1] data selection, meaning that any CsOH matter condensation will be increased by 36% at the same condensation temperature, in relation with the formation of liquid aerosols quantity.

The formation enthalpy of the dimer is deduced from our retained dissociation enthalpy and the preceding formation enthalpy of the monomer,

$$\Delta_f H^\circ(\text{Cs}_2\text{O}_2\text{H}_2, \text{g}, 298.15 \text{ K}) = -652.0 \pm 11.7 \text{ kJ} \cdot \text{mol}^{-1}. \quad (36)$$

The uncertainty is calculated using the compensation of errors relation. Gurvich *et al.* [1] adopted the value  $-653.0 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}$ , which is in good agreement with our value due to compensations in the thermodynamic cycles since their references are not the same as presently used. Indeed, Gurvich *et al.* [1] compared the dimer series –  $\text{K}_2\text{O}_2\text{H}_2$ ,  $\text{Rb}_2\text{O}_2\text{H}_2$  – as done by Schoonmaker and Porter [25] in which the rubidium hydroxide was already an estimated value.

In respect to the flame studies [38–40] we believe – (i) as Gurvich *et al.* [1] that “the high temperatures employed in studies of equilibria in flames resulted in significant uncertainties for the 3rd-law enthalpies of reaction”, due to the lack of knowledge of the exact electronic states of the  $\text{Cs(g)}$  and  $\text{CsOH(g)}$  species at high temperature, – (ii) also that temperature uncertainty remains very large according to the presently evaluated uncertainty of the real temperature of the flame and its internal gradients, – (iii) that the choice of reduced reactions sets remains particularly difficult to fix as presently analyzed by thermodynamics. In the case of flame study performed at rather low temperature and with different analytic detectors to ascertain the real measured reaction, the reliability of the results can be improved as it is the case for the Cotton and Jenkins [42] flame work. Indeed, the resulting formation enthalpy remains the closest ( $12 \text{ kJ} \cdot \text{mol}^{-1}$ ) to the conventional thermochemical retained enthalpy in this study.

Looking at the “recommendations for future measurements” proposed in the Gurvich *et al.* [1] compilation, the present work gives response to the item “Mass spectrometric study of potassium, rubidium, and cesium hydroxides to obtain reliable quantitative data on vapor composition, including relative concentration of trimeric, possibly tetrameric molecules”, and this presently for the only CsOH compound. Our main thermodynamic results concern:

- the melting temperature of the anhydrous CsOH compound
- the dimerization constant from monomer to dimer,
- the enthalpies of formation of these two species,
- the existence of the trimeric molecule in very small proportions (<0.01%) as proposed by Roki *et al.* [5].

Gurvich *et al.* [1] pointed out that the selected structure for the dimer would present some active modes in Raman spectra that should be detected as a structural confirmation. Some new results could modify the free energy function and, consequently, the dissociation energy of the dimer. As we did not observe any

systematic trends in our retained third law results, the modification of the free energy function would probably not be very important.

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