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Gaseous phase above Ru-O system: a thermodynamic data assessment

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Abstract

The present study is a critical assessment of thermochemical data for gaseous ruthenium oxides based on available experimental data. A full critical analysis and a reinterpretation of data are presented with a proposition for new accurate standard formation enthalpies values: $\Delta_f H^\circ_{298}(\text{RuO}_4, \text{g}) = -197.6 \pm 5.5 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ_{298}(\text{RuO}_3, \text{g}) = -53.0 \pm 10 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ_{298}(\text{RuO}_2, \text{g}) = 158 \pm 20 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ_{298}(\text{RuO}, \text{g}) = 301 \pm 28 \text{ kJ mol}^{-1}$.

Keywords: Thermodynamic data, Ru-O, gas phase, Entropy, Formation enthalpy, $\text{RuO}_4(\text{g})$, $\text{RuO}_3(\text{g})$, $\text{RuO}_2(\text{g})$, $\text{RuO}(\text{g})$, critical assessment

1 Introduction

Knowledge of the gas phase thermodynamic properties of the Ru-O binary system is important for at least three main applications: - (i) the corrosion behavior of Ru electrodes or $\text{RuO}_2(\text{s})$ catalytic coatings – (ii) the evaporation of some Ru species above 373 K during nitric acid treatment of the Ru containing burned nuclear fuels that have been supposed containing mainly $\text{RuO}_4(\text{g})$ or related molecules, or - (iii) in severe nuclear accident releases.

In the Ru- O_2 system, there exists two condensed oxides:

- (i) $\text{RuO}_2(\text{s})$ the thermodynamic properties of which have been recently compiled and assessed by Gossé et al [1] and Chatillon et al [2];
- (ii) $\text{RuO}_4(\text{s})$ that melts at room temperature and vaporizes with significant total vapor pressure at low temperature as determined by Nikol'ski (1964) [3].

The gas phase composition of the Ru-O system has been studied only above the Ru- RuO_2 range where the molecules of $\text{RuO}_4(\text{g})$, $\text{RuO}_3(\text{g})$, $\text{RuO}_2(\text{g})$ and $\text{RuO}(\text{g})$ are identified by independent spectroscopic methods and by quantum chemistry and their structure is given. In the last compilation made in 1990 by Cordfunke and Konings [4] the free energy functions have been only estimated because a lack of experimental values concerning the structural data of the molecules.

The present work improve this first selection of thermodynamic properties by taking into account more complete experimental data sets. In the first step of this study, a literature review of the structural properties of the gaseous molecules of Ru-O system and their thermodynamic functions is made. Then, starting with these selected values, new third law calculations are performed to propose more accurate values than those proposed in the last compilation [4].

1.1 Assessment of structures of RuO_n(n=1 to 4) gaseous molecules

First step in the thermodynamic knowledge of gaseous molecules is the determination of the structural properties of the molecules: their geometry (*i.e.* interatomic distances and bond angles), vibration frequencies, rotational constants as well as their electronic states.

Interatomic Ru-O distances in the gaseous molecules as well as methods of measurement and / or calculations come from Hamaka et al.[5], Siegbahn [6] , Miradji et al [7], Zhou et al [8], Krauss et Stevens [9], Schäfer et al. [10] and Scullman and Thelin [12]. Distances in the two varieties of RuO₄(s) solid crystal published by Pley and Wickleder [11] are considered (*see* Table 1 in *Appendix I*).

1.1.1 RuO₄(g) molecule

Molecular parameters of RuO₄(g) as proposed in literature and used throughout this work are **presented in Table I-2 in Appendix I**. The selected structure is a tetrahedral molecular structure, strictly regular (T_d), in agreement with that proposed by Greene et al [13]. Pley and Wickleder [11] by X-ray diffraction of RuO₄(s) crystal showed that the crystal is formed of tetrahedral entities with Ru-O distances ranging from 1.695 Å (cubic structure) to 1.701 Å (monoclinic structure).

Normally, the gaseous molecule has a more relaxed structure because there are no nearest neighbors, thus, RuO₄(g) would be similar to the most relaxed solid entity, *i.e.* the monoclinic. The geometry of the RuO₄(g) molecule was analyzed by Braune and Stute [14] by electron diffraction from molecular beam on the basis of a regular tetrahedron structure and then more recently by Schäfer et al. [10] with an improved technique. In the present study, the retained interatomic distance value for Ru-O in RuO₄ (g) is set as proposed by Schäfer et al [10] (*i.e.* $r_{\text{Ru-O}}$ with 1.7058 ± 0.003 Å) because it is considered as slightly relaxed (0.3%) as for the condensed phase when a monoclinic crystal structure is considered. Quantum calculations (*see Table I-2 in Appendix I*) give smaller values resulting in higher vibration frequencies (mainly verified with the normal symmetric vibration ν_1). Several authors determined the ν_3 (anti-symmetric) vibration frequency using IR spectroscopy (**Table I-2 in Appendix I**): experimental measurements are in agreement, around 920 cm⁻¹, meanwhile *ab-initio* calculations gave higher values ranging from 923 to 974 cm⁻¹. Generally, frequencies obtained by quantum or *ab-initio* calculations are higher than those measured because the calculated equilibrium interatomic distance is smaller than the measured one and these are related to a slightly greater force constant. After analysis of the band contours in spectroscopy, the complete set of experimental vibration frequencies proposed by McDowell et al [15] is retained in this work with the only vibration frequencies resulting from Ar matrix isolation. Indeed, those measured in the presence of Ne are discarded because they might be influenced by Van Der Waals interactions in the case of this rare gas with higher molar mass. The *ab-initio* frequency set calculated by Hamaka et al [5] and Miradji et al [7] confirms the present experimental selection while being slightly higher in relation with an interatomic Ru-O distance calculated shorter than from our selected experimental values. The selected ground electronic state is the one calculated by Miradji et al [7] ¹A₁ with a triplet state at an electronic level 14210 cm⁻¹ (1.76 eV).

1.1.2 RuO₃(g) molecule

Molecular parameters of RuO₃(g) as proposed in literature and used throughout this work are presented in **Table I-3 in Appendix I**. The structure of the RuO₃(g) molecule is planar type one

with 120° angle (D_{3h}). The only measured vibration frequency ν_3 by Kay et al [16] is rather confirmed by *ab-initio* calculations of Miradji et al [7] with some shift. The comparison of Ru-O interatomic distances between $\text{RuO}_4(\text{g})$ and $\text{RuO}_3(\text{g})$ (see **Table I-3 in Appendix I**) **obtained by various quantum chemistry calculations** shows that there is no (or very little) hybridization of the **released** electrons with those in other orbitals. Thus, the $\text{RuO}_3(\text{g})$ molecule keeps the same interatomic distance as in the saturated $\text{RuO}_4(\text{g})$ molecule. Consequently, in this study, the experimental interatomic distance proposed for $\text{RuO}_4(\text{g})$ was retained for the $\text{RuO}_3(\text{g})$ molecule and farther for $\text{RuO}_2(\text{g})$. The ground electronic state of $\text{RuO}_3(\text{g})$ selected is that calculated by Miradji et al [7] $^1\text{A}_1$ with a triplet state at an electronic level 5183 cm^{-1} (0.64 eV).

1.1.3 The $\text{RuO}_2(\text{g})$ molecule

Molecular parameters of $\text{RuO}_2(\text{g})$ as proposed in literature and used throughout this work are presented in **Table I-4 in Appendix I**. Two experiments of IR spectroscopy ([16], [8]) are in relative agreement and propose a C_{2v} type structure with a $150 \pm 2^\circ$ angle. Vibration frequencies (symmetric and anti-symmetric in the axis of the bonds) that was experimentally measured are in relative agreement, while *ab-initio* calculations give some higher symmetrical frequencies. These higher values reflect the downward trend in frequency measured when molecules are trapped in Ar or Ne matrix. The general trend shows small difference between the two experimental symmetrical frequencies ν_1 and anti-symmetric ν_3 - particularly determined by Kay et al [16] – in agreement with *ab-initio* work of Miradji et al [7]. Given this agreement and because the bending frequency ν_2 was not experimentally determined, the present study retains the value of ν_2 calculated by Miradji et al [7]. To be consistent between frequencies and interatomic distance, the value proposed by Miradji et al [7] is proportionally adjusted with the average ratio deduced from frequencies ν_1 and ν_3 . For the electronic state, the basic one is a singlet sigma $^1\text{A}_1$ type and, as proposed by two quantum calculations, there exists a triplet state at 334 cm^{-1} level. Since no other available experimental information exists, this study retains these values for the electronic states.

1.1.4 The $\text{RuO}(\text{g})$ molecule

Molecular parameters of $\text{RuO}(\text{g})$ as proposed in literature and used throughout this work are presented in **Table I-5 in Appendix I**. This study retains the values from atomic emission spectroscopy obtained by Scullman and Thelin [12], who already corrected the data of Raziunas et al [20]. *Ab-initio* calculations of Miradji et al [7], more refined than other previous calculations give interatomic distance and vibration frequency close to experimental values. The calculated Ru-O distance in the molecule $\text{RuO}(\text{g})$ shows a weakened bond due to the presence of **non-bonding orbitals**, which probably play a "repulsive" role (anti-bonding). This bond **length is consistent with** spectroscopic results (**Table I-1 and Table I-5 in Appendix I**). The **ground** electronic state selected takes into account the first level observed by spectroscopy.

1.2 Compilation of published gaseous molecules formation enthalpies

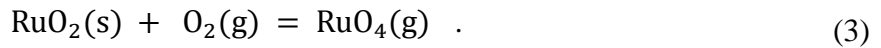
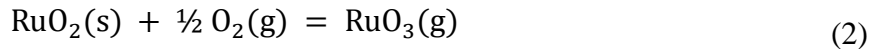
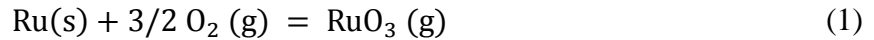
Thermodynamic studies of the Ru-O system gas phase stability have been carried out: - (i) using transpiration or transport methods **mainly for the study of RuO₄(g) and RuO₃(g) molecules**, - (ii) using mass spectrometry **for the study of RuO₂(g) and RuO(g) molecules**.

1.2.1 Works using transpiration methods

Schäfer et al [24-26] carried out three kinds of experiments:

- Heating a Ru filament in a controlled oxidizing atmosphere (the so-called “incandescent filament technique”) with evaluation of the filament mass loss by weighing before and after heating
- Continuous weighting with a thermo-balance of Ru samples subjected to oxidation and H₂ reduction cycles to evaluate the volatility of Ru oxides in relation to the Ru loss of the initial sample
- Total pressure measurement by a static method *i.e.* manometry at cold point (room temperature at walls).

In the incandescent filament technique, Ru loss of the filament is performed at two oxygen pressures for the same temperature (pyrometric monitoring of filament surface). Some experiments are carried out in sealed glass ampoules followed by a heat treatment. Ru mass losses allows the authors to determine the main vaporization reactions from the different proportions of Ru losses related to the O₂(g) pressure according to the following reactions,



At low temperature, the proportionality observed between the mass losses and the pressure p(O₂) (reaction (3)) indicates that RuO₄(g) molecule is in equilibrium with RuO₂(s) and that this molecule is predominant in the gas phase. Conversely, at high temperature RuO₃(g) predominates since the mass loss is proportional to pressure p(O₂)^{3/2} on Ru(s) and to pressure p(O₂)^{1/2} on RuO₂(s).

Schäfer et al [26] have published two tables (on pages 50 and 51) with the partial pressures of RuO₄(g) and RuO₃(g) and the equilibrium constants of reactions (2) and (3). Schäfer et al [26] selected two measurements at two temperatures – 1069K for RuO₄(g) – 1477K for RuO₃(g) - to deduce reaction (2) and (3) enthalpies. They estimated entropies of RuO₂(s) and Cp of RuO₃(g) and RuO₄(g) gaseous molecules to deduce enthalpies of reactions (2) and (3) at 298 K, then enthalpies of formation.

Bell and Tagami [27] confirm, by varying the oxygen content at different temperatures in a transpiration device, that the vapor is mainly composed of RuO₃(g) and RuO₄(g). Then, quantitative experiments are performed by method of transpiration under O₂ flow at one

atmosphere with a $\text{RuO}_2(\text{s})$ sample doped by a radiotracer. The mass transport of total Ru is performed by radiometric analysis of deposit at the output. It is assumed that the total transport is proportional to the sum $p(\text{RuO}_3) + p(\text{RuO}_4)$ according to reactions (2) and (3). The authors [27] estimated the proportions of $\text{RuO}_3(\text{g})$ and $\text{RuO}_4(\text{g})$ in the vapor from these mass losses according to relation,

$$p_{\text{RuO}_3} + p_{\text{RuO}_4} = A e^{C/T} + B e^{D/T} \quad (4)$$

in the temperature range 1075 - 1776 K and by an iterative method they determine all constants. These four constants are related to the enthalpies and entropies of reactions (2) and (3) and their fit is a general treatment based on 2nd law of thermodynamics that determines the enthalpy and entropy values of the two reactions at mean temperature.

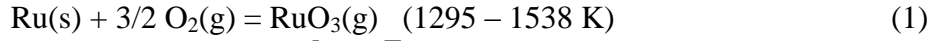
Penman and Hammer [28] performed a transpiration experiment with an oxygen carrier gas on a sample of $\text{RuO}_2(\text{s})$. The pressure of the oxygen, which is fed counter-currently in the furnace shell to the evaporation chamber, is determined by means of a mercury manometer, while the vapors of the gaseous oxides of Ru escape through a capillary tube and then condense in a glass wool. Deposits are then dissolved to analyze the transported amount of Ru by scintillation. Different capillary tube diameters are used to certify that the extracted gas is saturated within a flow range of a factor 10. However, the authors [28] do not give any indication on the differences observed nor on the determination of a plateau as a function of the carrier gas flow rate as is usually done in the transpiration method: constant determined pressure values correspond at least to part of the usual plateau. Based on the experiments of Schäfer et al [24-26] and a constant temperature test with different oxygen pressures, the authors proposed a vapor mainly composed of $\text{RuO}_4(\text{g})$ in their low temperature range *i.e.* 726 - 996 K.

1.2.2 Works using mass spectrometry

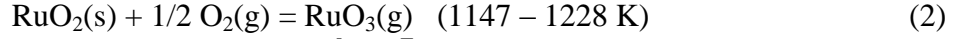
Tagirov et al [29] vaporized $\text{RuO}_2(\text{s})$ in quartz effusion cells between 980 and 1190 K and measure the O_2 pressure by mass spectrometry without detecting any other Ru-based gaseous species, probably due to insufficient mass spectrometry sensitivity. Indeed, according to Schäfer et al [26] and Bell and Tagami [27] $\text{RuO}_3(\text{g})$ and $\text{RuO}_4(\text{g})$ would have a proportion $\approx 10^{-3}$ to 10^{-4} **relatively to oxygen pressure**, a proportion that can be measured in the usual detection range of mass spectrometry using effusion cells.

To circumvent the sensitivity requirements of the mass spectrometer and promote the dissociation of complex gaseous oxides, Norman et al [23] carried out a mass spectrometric study using an effusion cell equipped with an O_2 gas flow inlet to stabilize the oxygen potential by compensating for the preferential oxygen lost by effusion. For low temperature studies (< 1500 K), the sample is pure Ru **placed** in a quartz cell, and for higher temperatures the authors [23] use an alumina cell. The $\text{O}_2(\text{g})$ pressure in the cell has been set at about 10^{-4} bar (this 10^{-4} bar, we assume, must be the usual upper pressure limit for the effusion method) according to the authors' [23] estimates and they can vary it by a factor 10 (probably below 10^{-4} bar). The authors [23] analyzed the slope of the measured ionic intensities of RuO_3^+ , RuO_2^+ and RuO^+ at low temperature as a function of the variation in the oxygen potential $p(\text{O}_2) \approx \text{intensity}(\text{O}_2^+)$ and they observed a break indicating the transformation of the sample from $\text{Ru}(\text{s})$ to $\text{RuO}_2(\text{s})$. In the low temperature range,

they study the following reactions that produce $\text{RuO}_3(\text{g})$ which is the main detected gaseous species,



$$K_p(1) = \frac{p_{\text{RuO}_3}}{a_{\text{Ru}} \cdot p_{\text{O}_2}^{3/2}} \approx \frac{I_{\text{RuO}_3^+} T}{1 \cdot (I_{\text{O}_2^+} \cdot T)^{3/2}} \approx I_{\text{RuO}_3^+} \cdot T^{-1/2} \quad (5)$$



$$K_p(2) = \frac{p_{\text{RuO}_3}}{a_{\text{RuO}_2} \cdot p_{\text{O}_2}^{1/2}} \approx \frac{I_{\text{RuO}_3^+} T}{1 \cdot (I_{\text{O}_2^+} \cdot T)^{1/2}} \approx I_{\text{RuO}_3^+} \cdot T^{1/2}. \quad (6)$$

These reactions correspond to two different slopes over the entire temperature range when working at a constant ion intensity $I(\text{O}_2^+)$. These slopes (Figure 2 of Norman et al [23]) give the enthalpies (2nd law method) of reactions (2) and (3).

At higher temperature, using an alumina cell, the molecule $\text{RuO}_3(\text{g})$ is totally decomposed - disappearance of the RuO_3^+ ion intensity in the mass spectrum - and the authors [23] observe the evolution of RuO_2^+ , RuO^+ and Ru^+ ion intensities as a function of the oxygen potential followed by the O^+ coming from the dissociation of oxygen at high temperature according to the reaction,



As the proportion of $\text{O}(\text{g})$ varies with temperature, the authors [23] monitor the main reactions involving $\text{O}_2(\text{g})$ (i.e. O_2^+ ionic intensities) which can be maintained at a constant value when the flow of incoming oxygen is adjusted. Indeed, maintaining the intensity of O_2^+ as a constant value at a given temperature does not allow determining the sensitivity of the mass spectrometer for this species. Based on the assumption of a constant O_2^+ ion intensity, the slopes reflect the following main vaporization reactions,



$$K_p(7) = \frac{p_{\text{RuO}_2}}{a_{\text{Ru}} \cdot p_{\text{O}_2}} \approx \frac{I_{\text{RuO}_2^+} T}{1 \cdot I_{\text{O}_2^+} T} \approx I_{\text{RuO}_2^+} \quad (9)$$



$$K_p(9) = \frac{p_{\text{RuO}}}{a_{\text{Ru}} \cdot p_{\text{O}_2}^{1/2}} \approx \frac{I_{\text{RuO}^+} T}{1 \cdot (I_{\text{O}_2^+} \cdot T)^{1/2}} \approx I_{\text{RuO}^+} \cdot T^{1/2}. \quad (11)$$

Oxygen potential $p(\text{O}_2)$ remains fixed at 10^{-4} bar (estimated by the authors) whatever the temperature, and the 2nd law (slope) gives the enthalpies of the above reactions.

The parent ion Ru^+ (measured at an ionization voltage of 10 V to eliminate any contribution of dissociative ionization of the gaseous oxide species) is not sensitive to oxygen pressure as long as $\text{RuO}_2(\text{s})$ is not formed. Indeed, its origin is only due to the vaporization of the sample $\text{Ru}(\text{s})$ as $\text{Ru}(\text{g})$ with an oxygen solubility in $\text{Ru}(\text{s})$ considered negligible (see Chatillon et al [2]). The authors registered the logarithm of the products $I_{\text{Ru}^+} \cdot T$ (in mass spectrometry, these products are

proportional to the pressure of Ru) with respect to the inverse of temperature and, then, calibrated their spectrometer on the known pressure of pure Ru to obtain the mass spectrometer sensitivity related to Ru(g). Further, sensitivities for oxides are calculated using the maximum ionization cross-section (at 75 V) as proposed by Otvos and Stevenson [30] - but applied to their measurement at very low potentials *i.e.* close to the ionization threshold - and have estimated the efficiency of the multiplier (efficiency(yield) $\approx 1/\sqrt{\text{Molar Mass of the ion}}$). They not provide any of their estimated values to re-calculate their sensitivity. However, the use of the maximum ionization cross-sections for such very low ionization potentials can lead to large uncertainties (≈ 2 to 5 times the value of the ion ratios between the different species). Their calibration of the spectrometer leads to the evaluation of the equilibrium constants K_p (not published) and consequently the published Gibbs energies which allow the calculation of the reaction entropies at medium temperature by the relation,

$$\Delta_r S_T^\circ = R \ln K_p + \frac{\Delta_r H_T^\circ}{T}. \quad (12)$$

using their published 2nd law reaction enthalpies $\Delta_r H_T^\circ$.

2 Results

In this **part** accurate values for the “thermal” functions (*i.e.* C_p° (298K), S_{298}° , $H_{298}^\circ - H_0^\circ$, - $(G_T^\circ - H_0^\circ)/T$) allow **new and improved** third law calculations of the enthalpies of formation for RuO₄(g), RuO₃(g), RuO₂(g) and RuO(g).

2.1 “Thermal” functions for the gaseous species

From the literature data presented previously and with our selected molecular parameters for RuO₄(g), RuO₃(g), RuO₂(g) and RuO(g), and using relations proposed in Janaf tables [31] (Rigid Rotator, Harmonic Oscillator) the basic standard data for the “thermal” functions (*i.e.* C_p° (298K), S_{298}° , $H_{298}^\circ - H_0^\circ$, - $(G_T^\circ - H_0^\circ)/T$ and - $(G_T^\circ - H_{298}^\circ)/T$) are presented in Table 1 to **Table 4** and compared with those stored in data banks.

Table 1. Heat capacity values for gaseous molecules of Ru-O system (RuO(g), RuO₂(g), RuO₃(g), RuO₄(g)) from selected parameters.

Molecule	C_p° (298.15 K) / J K ⁻¹ mol ⁻¹			
	This work	SGPS-SGTE [32]	TDNucl[33]	Cordfunke and Konings [4]
RuO ₄ (g)	75.188	75.814	75.596	75.188*
RuO ₃ (g)	61.605	59.404	59.354	61.605*
RuO ₂ (g)	50.155	56.483	56.422	44.093*
RuO(g)	31.503	31.358	31.463	31.544

*Calculated value from Cordfunke and Konings [4] molecular parameters

Table 2. Entropy at 298K issued from the present assessment compared to the preceding studies.

Molecule	S°_{298} / J K ⁻¹ mol ⁻¹				
	This work	Cordfunke and Konings [4]	Miradji et al [7] Ab-initio	SGPS-SGTE [32]	TDNucl[33]
RuO ₄ (g)	280.846	280.846*	287.5	290.772	290.101
RuO ₃ (g)	283.198	267.905*	291.0	276.253	276.143
RuO ₂ (g)	258.938	259.162*	266.4	267.542	267.430
RuO (g)	238.138	242.212*	242.3	242.175	242.063
Ru(g)	186.4 [4]	186.4*	186.6	190.946	191.055

*Calculated value from Cordfunke and Konings [4] molecular parameters

Table 3. Enthalpy increments $H^{\circ}(298.15) - H^{\circ}(0)$ issued from the present assessment compared to the preceding studies.

Molecule	$H^{\circ}(298.15) - H^{\circ}(0)$ / J mol ⁻¹			
	This work	SGPS-SGTE [32]	TDNucl[33]	Corfunke and Konings [4]
RuO ₄ (g)	15512.4	No available data	No available data	15512.4*
RuO ₃ (g)	14618.5			14618.5*
RuO ₂ (g)	13237.2			11197.6*
RuO(g)	8846.6			8851.2*

*Calculated value from Cordfunke and Konings [4] molecular parameters

Table 4. Free energy function referred to 0K issued from the present assessment compared to the preceding studies.

Molecule	$-(G^{\circ}_T - H^{\circ}_0)/T$ at T=298.15K / J K ⁻¹ mol ⁻¹			
	This work	SGPS-SGTE [32]	TDNucl [33]	Corfunke and Konings [4]
RuO ₄ (g)	228.817	238.743*	238.073*	228.817*
RuO ₃ (g)	234.168	227.222*	227.113*	234.168*
RuO ₂ (g)	223.459	223.144*	223.033*	221.605*
RuO(g)	208.466	212.503*	212.392*	212.525*

*Calculated using our value $H^{\circ}(298.15) - H^{\circ}(0)$ from Table 3

To evaluate the impact of some of our parameter choices on the uncertainties – coming from interatomic distance and the electronic levels calculated by quantum chemistry - we performed several calculations of the free energy function $F_e^{\circ}_T$ used in third law calculations. Comparison

of the relative difference between the different Fef°_T calculations with these various parameters - gives an idea of the expected accuracy related to our selection. The calculated differences are:

- $\text{RuO}_4(\text{g})$: +0.16% maximum at 6000 K taking into account the Triplet at 14210 cm^{-1} instead of a simple sigma state without this level at 14210 cm^{-1} .
- $\text{RuO}_3(\text{g})$: +1.17% maximum at 6000 K taking into account or not the Triplet state at 5183 cm^{-1} and from -0.1 to -0.06% between 298K and 6000 K when the interatomic distance decreases towards ab-initio calculations.
- $\text{RuO}_2(\text{g})$: +3.4 to +3.0% maximum between 298 K and 6000 K taking into account the Triplet state at 334 cm^{-1} and from -0.1 to -0.08% when the distance decreases towards the ab-initio calculations.
- $\text{RuO}(\text{g})$: classical precision of $\pm 0.1\%$ at 298 K for a molecule defined by spectroscopy determinations and up to 5% in the range 4000-5000 K (see Gurvich et al [34]).

2.2 Formation enthalpies for the gaseous phase

In this part are exposed new third law calculations performed to obtain formation enthalpies for gaseous molecules $\text{RuO}_4(\text{g})$, $\text{RuO}_3(\text{g})$, $\text{RuO}_2(\text{g})$, $\text{RuO}(\text{g})$ using original literature data from transpiration methods and mass spectrometry.

2.2.1 Improved results from works using transpiration methods

2.2.1.1 Works of Schäfer et al (1961-1963)

Compiling Schaffer et al [26] work the present analysis concluded that $\text{RuO}_4(\text{g})$ is the main molecule for temperatures $<1327\text{K}$ and that $\text{RuO}_3(\text{g})$ is predominant at higher temperatures. Besides, our so-called “thermal” thermodynamic functions selected for molecules RuO_3 and RuO_4 are very different from those estimated by Schäfer et al [26]. Then, we can recalculate the 3rd law enthalpies using their total pressure data [26] i.e. values presented in their Table 3 p. 47, and in pages 50 and 51. This calculation has been done already by Cordfunke and Konings [4] in their compilation.

To improve the accuracy in the determination of formation enthalpies of the two molecules $\text{RuO}_3(\text{g})$ and $\text{RuO}_4(\text{g})$, we resume the analysis of all initial experimental values by using generalized 3rd law calculations on the full data set and in particular by using the total pressure of Ru species at the same time, i.e. $\text{RuO}_3(\text{g}) + \text{RuO}_4(\text{g})$ pressure. The experimental raw values are temperature, imposed oxygen pressure and the ratio between the lost moles of $\text{RuO}_2(\text{s})$ and the elapsed moles of oxygen, corresponding to the volume of the carrier gas. Starting from their Table 3 p. 47 of reference [26], the number of moles of $\text{RuO}_2(\text{s})$ consumed is related to the number of moles of O_2 that flushed the reactor during a certain time. Thus, the volume V of gas O_2 (V_{O_2}) that carried away the oxide $\text{RuO}_4(\text{g})$ will give – according to the stoichiometry of reaction (3) - the loss of a number of moles n' of $\text{RuO}_2(\text{s})$ applying the ideal gas law,

$$p_{\text{RuO}_4} V_{\text{O}_2} = n_{\text{RuO}_4} RT = n'_{\text{RuO}_2(\text{s})} RT \quad (13)$$

and for oxygen

$$p_{\text{O}_2} V_{\text{O}_2} = n_{\text{O}_2} RT \quad (14)$$

that gives for reaction (3), the ratio

$$\frac{p_{RuO_4}}{p_{O_2}} = \frac{n'_{RuO_2}}{n_{O_2}}. \quad (15)$$

This relationship assumes that the pressure of $RuO_4(g)$ is relatively low compared to that of O_2 ($< 1\%$ as an upper value) so that the volume of gas V counted as the volume of O_2 is not significantly changed. The equilibrium constant of the reaction (3) will be then:

$$K_p(3) = \frac{p_{RuO_4}}{p_{O_2}} = \frac{n'_{RuO_2}}{n_{O_2}}. \quad (16)$$

For reaction (2) and according to its stoichiometry and with the measured volume of oxygen swept over the sample, thus the number of gaseous moles transported is,

$$p_{RuO_3} V_{O_2} = n_{RuO_3} RT = n''_{RuO_2(s)} RT \quad (17)$$

$$p_{O_2} V_{O_2} = n_{O_2} RT \quad (18)$$

n'' being, for the same experiment, the number of moles of $RuO_2(s)$ or Ru lost in the $RuO_3(g)$ vaporization for the same O_2 volume. This volume V_{O_2} is eliminated and the ratio of the pressures remains equal to the ratio of the number of moles,

$$\frac{p_{RuO_3}}{p_{O_2}} = \frac{n''_{RuO_2}}{n_{O_2}} \quad (19)$$

and reaction (2) equilibrium constant becomes:

$$K_p(2) = \frac{p_{RuO_3}}{\sqrt{p_{O_2}}} = \frac{p_{RuO_3}}{p_{O_2}} \cdot \sqrt{p_{O_2}} = \frac{n''_{RuO_2}}{n_{O_2}} \cdot \sqrt{p_{O_2}} \quad (20)$$

Thus, the total number of moles of $RuO_2(s)$ lost for the same volume of oxygen will be the sum $n' + n''$. Introducing n' and n'' in the previous relationships, $\frac{n_{RuO_2}}{n_{O_2}}$ becomes

$$\frac{n_{RuO_2}}{n_{O_2}} = \frac{n' + n''}{n_{O_2}} = \frac{p_{RuO_3} + p_{RuO_4}}{p_{O_2}}. \quad (21)$$

Schäfer et al [26] calculate directly from their experimental measured ratio $\frac{n_{RuO_2}}{n_{O_2}}$ the final ratio $\frac{p_{RuO_3} + p_{RuO_4}}{p_{O_2}}$ (as published in their Table 3).

Thus, we resume the analysis by checking the ratio of the pressures corresponding to relation (21) with respect to the molar ratio determined in the experiment. The partial pressures in relation (21) are calculated by applying the following two relations of the 3rd law of thermodynamics for reactions (2) and (3),

$$\Delta_{reac.2} H_{298}^\circ = -RT \ln K_2 + T \Delta_{reac.2} Fef_T^\circ \quad (22)$$

$$\Delta_{reac.3} H_{298}^\circ = -RT \ln K_3 + T \Delta_{reac.3} Fef_T^\circ \quad (23)$$

and

$$\ln K_2 = \frac{p_{RuO_3}}{p_{O_2}^{1/2}} = \frac{-\Delta_{\text{reac.2}}H_{298}^\circ + T \Delta_{\text{reac.2}}Fef_T^\circ}{RT} \quad (24)$$

$$\ln K_3 = \frac{p_{RuO_4}}{p_{O_2}} = \frac{-\Delta_{\text{reac.3}}H_{298}^\circ + T \Delta_{\text{reac.3}}Fef_T^\circ}{RT}. \quad (25)$$

Partial pressures in these relationships are expressed in bar. Then, using the oxygen pressures and temperatures of Schäfer et al [26] (from their Table 3), we calculate the pressures of $RuO_3(g)$ and $RuO_4(g)$ using our selected free energy functions and arbitrary values for the standard reaction enthalpies. The values of standard enthalpies of the reaction (2) and (3) at 298 K calculated at two extreme temperatures by Schäfer et al. [27] are used as initial values. Consistency between our calculations of partial pressures by 3rd law and the molar ratio experimental values is checked with relation (21) as a function of temperature. For the initial enthalpies as determined by Schäfer et al [26] we observe at low temperatures - where $RuO_4(g)$ is the main species - a small relative difference between the two ratios in relation (21) showing that the value of enthalpy of the reaction (3) at 298 K is quite correct. At high temperatures, the difference is much larger, showing that the initial chosen enthalpy of the reaction (2) is wrong. Next, the standard enthalpies at 298 K for reactions (2) and (3) are taken as variable parameters to check relation (21). By varying the two reaction enthalpies in steps - method of trial and error - we obtain a data set (see for example Figure 1) in which the deviation is minimized over the entire experimental temperature range of Schäfer et al [26]. **This minimum is observed for reaction (2) enthalpy fixed at the value proposed below from Penman and Hammer work [28] although the minimum deviation is not very sensitive to variations around this retained value.** The deviation also remains more pronounced for high temperatures, *i.e.* in the range where Schäfer et al [26] proposed $RuO_3(g)$ as the main molecule. This deviation is **more pronounced also in relation to scattered experimental data for instance taken at the same temperature.** Moreover, according to enthalpies variation tests, it follows that reaction (2) has greatest influences on the deviations between the experimental moles ratio and the calculated partial pressures ratio (relation (21)).

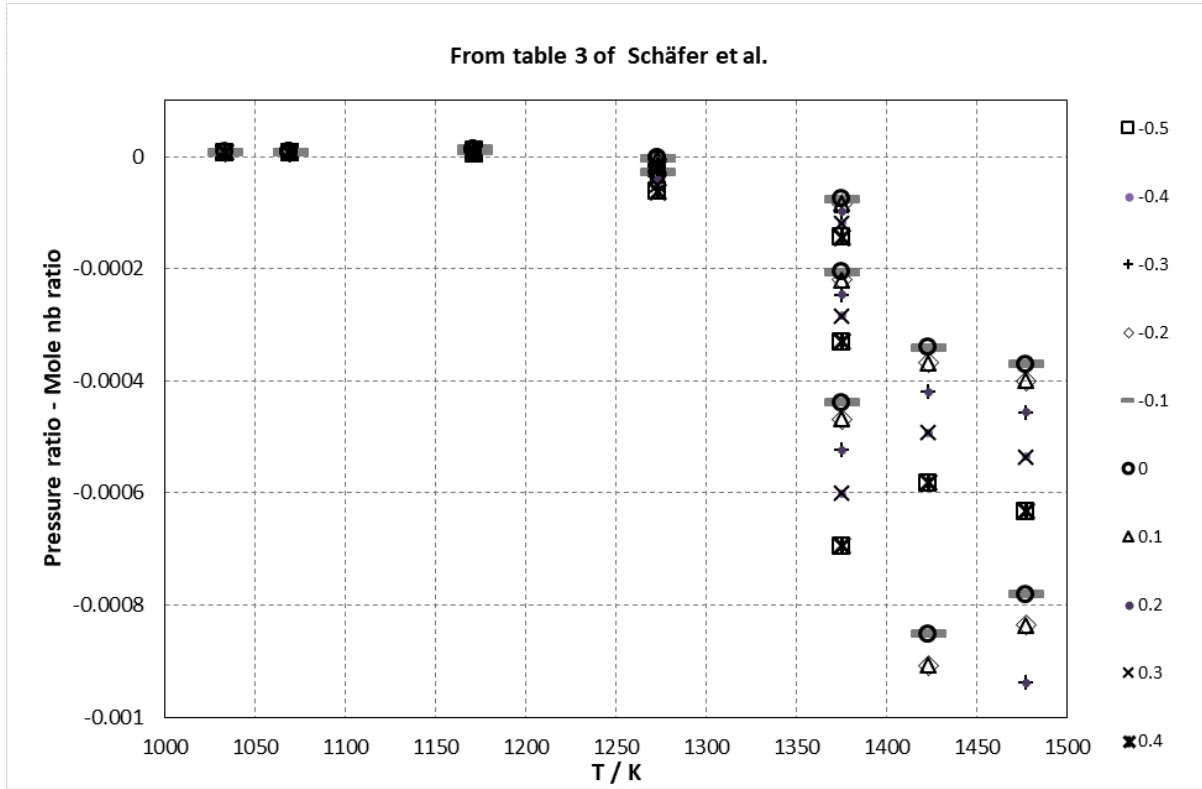


Figure 1: Evolution of the difference between the ratio of the partial pressures ($RuO_3(g) + RuO_4(g) / O_2(g)$) calculated via the 3rd law and the ratio of the experimental number of moles published by Schäfer et al [26] (see above relation (21)) as a function of temperature. In the present figure, the numbers at the right side correspond to an index for the variation of the enthalpy of reaction (2) when the enthalpy of reaction (3) is fixed.

The best values of reaction enthalpies that verify relation (21) are,

$$\Delta_{\text{reac.2}} H_{298}^{\circ}(\text{final}) = 257716 \text{ J mol}^{-1} \quad (26)$$

$$\Delta_{\text{reac.3}} H_{298}^{\circ}(\text{final}) = 114700 \text{ J mol}^{-1} \quad (27)$$

These new reactions enthalpies lead to the best standard formation enthalpies of $RuO_3(g)$ and $RuO_4(g)$ from the data set of Schäfer et al [26], using our selected formation enthalpy for $RuO_2(s) = -312.3 \text{ kJ mol}^{-1}$ [2],

$$\Delta_f H_{298}^{\circ}(RuO_3, g) = -54.6 \pm 8.0 \text{ kJ mol}^{-1} \quad (28)$$

$$\Delta_f H_{298}^{\circ}(RuO_4, g) = -197.6 \pm 10.0 \text{ kJ mol}^{-1} \quad (29)$$

Total uncertainty includes the uncertainty values in the calculations of 3rd law due to the free energy functions of gaseous species and the sensitivity observed in the method of trial and error to seek the minimum deviation from the two enthalpies taken as variable parameters.

2.2.1.2 Works of Bell and Tagami (1963)

Bell and Tagami's [27] entropy 2nd law results (Table 5) are compared with the values calculated from our selected entropies. Their reaction entropies are clearly different from the accurate ones we have selected reflecting first the uncertainties associated with their 2nd law treatment.

Table 5. Comparison of entropies of reactions (2) and (3) determined with 2nd law treatment by Bell and Tagami [27] and our values independently calculated.

Studied reaction	Bell et Tagami [27]			This work
	T _{mean} /K	$\Delta_r H^\circ$ (T _{mean}) / kJ mol ⁻¹	$\Delta_r S^\circ$ (T _{mean}) / J K ⁻¹ mol ⁻¹	$\Delta_r S^\circ$ (T _{mean}) / J K ⁻¹ mol ⁻¹
$\text{RuO}_2(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{RuO}_3(\text{g})$	1400	214.2 ± 4.2	94.1 ± 4.2	102.321
$\text{RuO}_2(\text{s}) + \text{O}_2(\text{g}) = \text{RuO}_4(\text{g})$	1400	94.1 ± 8.4	-0.84 ± 8.4	3.167

In order to determine the enthalpy values at 298 K we performed the same 3rd law treatment as in the case of Schäfer et al [26] data. Our calculations start from the original determinations published by Bell and Tagami [27] in their Table I: from the total pressure observed (column 2) associated with the loss of Ru by transport during their experiment, they converted to the sum (p(RuO₃(g)) + p(RuO₄(g)) under an oxygen pressure of 1 atm. In fact, this sum is directly related to the number of RuO₂(s) moles lost in the oxygen stream as shown in relation (21). In this study, we use the following relationship for the mole ratio,

$$\frac{n_{\text{RuO}_2}}{n_{\text{O}_2}} = \frac{p_{\text{RuO}_3} + p_{\text{RuO}_4}}{p_{\text{O}_2}} \text{ (from Bell and Tagami)} \quad (30)$$

where the sum of partial pressures are from table I column 2 issued from Bell and Tagami [27] for an oxygen pressure of 1atm. In our calculations, we observed that data at T > 1600 K never satisfy relation (21) whatever the arbitrary enthalpies introduced for reactions (2) and (3). Moreover, **further** thermodynamic calculations performed with the **present work** selected values showed that for T > 1600K, equilibrium was established with Ru(s) and reactions (2) and (3) do not take place. **Same features are observed for deviation and scatter as for Schaffer et al [26].** Finally, we retain the data at T < 1600K, and the enthalpies of the reactions deduced from the Bell and Tagami [27] transpiration data, are:

$$\Delta_{\text{reac.2}} H_{298}^\circ = 260940 \text{ J mol}^{-1} \quad (31)$$

$$\Delta_{\text{reac.3}} H_{298}^\circ (\text{final}) = 114700 \text{ J mol}^{-1}. \quad (32)$$

These new enthalpies of reactions lead to the standard formation enthalpies of RuO₃(g) and RuO₄(g), using our selected formation enthalpy for RuO₂(s) = -312.3 kJ mol⁻¹ [2],

$$\Delta_f H_{298}^\circ (\text{RuO}_3, \text{g}) = -51.4 \pm 8.0 \text{ kJ mol}^{-1} \quad (33)$$

$$\Delta_f H_{298}^\circ (\text{RuO}_4, \text{g}) = -197.6 \pm 10.0 \text{ kJ mol}^{-1}. \quad (34)$$

2.2.1.3 Works of Penman and Hammer (1968)

From Penman and Hammer [28] data and their hypothesis of the only $\text{RuO}_4(\text{g})$ in the vapor phase, our 2nd and 3rd laws calculations of reaction enthalpy for reaction (3) give:

$$\Delta_{\text{reac}} H_{298}^{\circ}(\text{2nd law}) = 109.1 \pm 7.1 \text{ kJ mol}^{-1} \quad (35)$$

$$\Delta_{\text{reac}} H_{298}^{\circ}(\text{3rd law}) = 114.7 \pm 2.5 \text{ kJ mol}^{-1} \quad (36)$$

Then, using our reference value for $\text{RuO}_2(\text{s})$, the 3rd law standard formation enthalpy of the $\text{RuO}_4(\text{g})$ molecule is

$$\Delta_f H_{298}^{\circ}(\text{RuO}_4, \text{g}) = -197.6 \pm 5.5 \text{ kJ mol}^{-1}. \quad (37)$$

Applying the same 3rd law calculation method as for data of Schäfer et al [26] and Bell and Tagami [27] - taking into account of the two species $\text{RuO}_3(\text{g})$ and $\text{RuO}_4(\text{g})$ in the vapor transport - we observe that calculations from the ratio $\frac{n_{\text{RuO}_2}}{n_{\text{O}_2}}$ are not sensitive to the variation of formation enthalpy of the $\text{RuO}_3(\text{g})$ molecule from -50 to 0 kJ mol^{-1} . We conclude that the $\text{RuO}_4(\text{g})$ molecule is surely the main species present in the vapor.

2.2.1.4 Retained thermodynamic data for $\text{RuO}_4(\text{g})$ and $\text{RuO}_3(\text{g})$ molecules

In the previous compilation, Cordfunke and Konings [4] directly apply 3rd law calculations to published raw partial pressures that lead to large variations in the enthalpies of formation, (-179 to -190 kJ mol^{-1} for $\text{RuO}_4(\text{g})$, and -60 to -65 kJ mol^{-1} for $\text{RuO}_3(\text{g})$) with a different reference for $\text{RuO}_2(\text{s})$. In the present work, the generalized interpretation by the 3rd law using **more accurate** free energy functions leads to very close enthalpy results whatever are the authors, a characteristic that is consistent with the usual accuracy of the transpiration method.

The retained value (quoted in table 10) with its uncertainty for $\text{RuO}_4(\text{g})$ comes from Penman and Hammer [28] meanwhile the retained value for $\text{RuO}_3(\text{g})$ is the mean value from Schäfer et al [26] and Bell and Tagami [27] the uncertainty being increased by half their enthalpy difference.

2.2.2 Improved results from works using mass spectrometry

Reaction entropies proposed by Norman et al [23] are compared to our calculated reaction entropies in Table 6.

Table 6. Entropies of different reactions derived by Norman et al [23] from their 2nd law calculations and comparison with our selected values

Reaction	$\Delta_{\text{reaction}} S_T^{\circ} / \text{J K}^{-1} \text{mol}^{-1}$		T range / K
	Mean T value Norman et al. [23]	This work	
$\text{Ru(s)} + 3/2 \text{O}_2(\text{g}) = \text{RuO}_3(\text{g})$	-87.027	-56.2 to -56.5	1295 -1538
$\text{Ru(s)} + \text{O}_2(\text{g}) = \text{RuO}_2(\text{g})$	-6.276	22.1 to 18.1	1740 - 2040
$\text{Ru(s)} + 1/2 \text{O}_2(\text{g}) = \text{RuO}(\text{g})$	49.371	89.7 to 86.7	1870 - 2020

Reaction entropy values at mean experimental temperatures deduced from the experiments by Norman et al [23] clearly disagree with those selected in the same temperature range in this work based on independent determinations of the molecular parameters of gaseous oxides. These discrepancies can come from three different sources: - (i) uncertainties in the calibration of their spectrometer associated with estimates of ionization cross sections (for evaluation of K_p), - (ii) derived 2nd law enthalpies with large uncertainties due to the small temperature ranges for the measurements, or – (iii) out-of-equilibrium steady-state vaporization in their Knudsen cell in relation to evaporation coefficients for at least one of the gaseous species. Consequently, 2nd law enthalpy values proposed by Norman et al [23] cannot be retained and, moreover, no evaluation of their associated uncertainty can be performed. A discussion on the high probability of low evaporation coefficients in the study by Norman et al [23] is presented in *Appendix II*.

Ionization processes and Born-Haber thermodynamic cycles

In mass spectrometry studies, identification of species in the gas phase is carried out by monitoring ionization efficiency curves and from the evolution of ions ratios as a function of temperature or composition that allows identifying the molecular origin of the detected ions. At this stage, a combination of different ionization processes can be used to deduce enthalpies for bond breaking using Born-Haber thermodynamic cycles:

- (i) Using adiabatic ionization: the appearance potential (AP) is the potential threshold above which an ion is formed. It is characterized by the ionization potential (IP) for a molecular ion (formerly called "parent" ion),
- (ii) Using dissociative ionization: when a bond break is directly observed from the appearance potential of ions formed (called “fragment ion”) or deduced from certain breaks in the ionization efficiency curves. It is characterized by its appearance potential (AP).

For the Ru-O system, different ions as determined in literature by mass spectrometry are presented in Table 7.

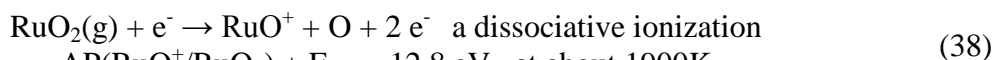
Table 7. Ionization and appearance potentials of ions determined by mass spectrometry and their proposed molecular precursors according to literature.

Authors (year) reference	Detected Ions	Appearance potential / V	Molecular Origin	Comments
Dillard et Kiser (1965)[35]	RuO_4^+	12.3 ± 0.2	RuO_4	Molecular ion
	RuO_3^+	15.7 ± 0.3	$\text{RuO}_4 + \text{RuO}_3?$	Most abundant on $\text{RuO}_4(\text{liq})$ Fragment + Molecular ion?
	-	-		
	RuO_2^+	14.2 ± 0.2	RuO_4	Fragment Ion
	RuO^+	18.1 ± 0.3	RuO_4	Fragment Ion
Norman et al (1968) [23]	Ru^+	22.3 ± 0.3	RuO_4	Fragment Ion
	RuO_4^+	12.8*	RuO_4	Molecular ion
	RuO_3^+	11.2	RuO_3	Molecular ion

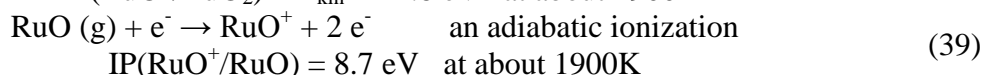
	RuO_2^+	10.6	RuO_2	Molecular ion
	RuO^+	8.7	RuO	Molecular ion
	Ru^+	7.7	Ru	Molecular ion
	Ru^+	13.0	RuO_2	Fragment ion
	RuO^+	12.8	RuO_2	Fragment ion

* ± 0.1 eV our estimate for Norman et al [23].

Norman et al [23] observed breaks in the ionization efficiency curves of Ru^+ and RuO^+ for a vapor containing essentially $\text{RuO}_2(\text{g})$. From the measured appearance energy of RuO^+ ion, the following cycle is used:



$$\text{AP}(\text{RuO}^+/\text{RuO}_2) + E_{\text{kin}} = 12.8 \text{ eV} \quad \text{at about 1900K}$$



$$\text{IP}(\text{RuO}^+/\text{RuO}) = 8.7 \text{ eV} \quad \text{at about 1900K}$$

where AP is for appearance potential, IP for the ionization potential and E_{kin} is for any kinetic energy associated to the neutral species O, a feature that cannot be observed by mass spectrometry. The difference (38)-(39) leads to,

$$\begin{aligned} \text{RuO}_2(\text{g}) &= \text{RuO}(\text{g}) + \text{O}(\text{g}) \\ \Delta_{\text{diss.}} H^\circ(\text{RuO}-\text{O}) + E_{\text{kin}} &= 4.1 \text{ eV} \end{aligned} \quad (40)$$

and

$$\Delta_{\text{diss.}} H^\circ_{1900\text{K}}(\text{RuO} - \text{O}) + E_{\text{kin.}} = 395.6 \pm 13.6 \text{ kJ mol}^{-1} \quad (41)$$

$$\text{Or } \Delta_{\text{diss.}} H^\circ_{1900\text{K}}(\text{RuO} - \text{O}) \leq 395.6 \pm 13.6 \text{ kJ mol}^{-1} \quad (42)$$

The cycles calculated from the molecules $\text{RuO}_4(\text{g})$ and $\text{RuO}_2(\text{g})$ are compared to final retained thermodynamic values of this work in *Table 8*. It should be noted that there is no value for an Ru^+ ion coming from $\text{RuO}(\text{g})$ and, therefore, no direct evaluation of the atomization energy of $\text{RuO}(\text{g})$.

Table 8. Dissociation enthalpies of different Metal-Oxygen bonds for the molecules $\text{RuO}_4(\text{g})$ and $\text{RuO}_2(\text{g})$ determined from ionization processes (adiabatic and dissociative) calculated at 298 K and comparison with the thermochemical values calculated from the formation enthalpies values, analyzed in this work.

Method	Energy from the Ionization processes		Energy from thermochemistry (retained in this work)	
Bond break / From molecule	$\Delta_{\text{diss}} H^\circ(\text{T})$ / kJ mol^{-1}	$\Delta_{\text{diss}} H^\circ(298\text{K})$ / kJ mol^{-1}	$\Delta_{\text{diss}} H^\circ(298\text{K})$ / kJ mol^{-1}	Authors / ref
$\text{RuO}_3\text{-O} / \text{RuO}_4(\text{g})$	≤ 482.4	$\leq 481.4 \pm 20$	393.8 ± 11.4	From retained values in this work
			384	Ab-initio, Miradji et al

				[7] in their Table 8
RuO – O /RuO ₂ (g)	≤ 395.6	$\leq 391.5 \pm 20$	392 \pm 20	From retained values in this work (Table 10)
			528	Miradji et al [7] in their Table 8
Ru – 2O/ RuO ₂ (g)	≤ 511.4	$\leq 490.6 \pm 20$	1003.4 \pm 20	This work in Table 90 and Cordfunke and Konings [4] for $\Delta_f H^\circ(\text{Ru}, \text{g})$
Or Ru – O ₂ / RuO ₂ (g)	≤ 511.4	$\leq 490.6 \pm 20$	505 \pm 20	

For molecule RuO₄(g), bond breaking energy RuO₃-O measured by mass spectrometry suggest a large contribution of kinetic energy (≈ 0.9 eV) since the calculated thermochemical value is accurate. For the ionization of the RuO₂(g) molecule, the dissociative ionization process giving O₂(g) instead of 2 O(g) seems more probable because the thermochemical value cannot be higher than the one deduced from the ionization process. Note that for the breaking processes of the RuO₂(g) molecule into RuO(g)+O(g), calculated values from thermodynamics and ionization process agree since the ionization process value has been further used (see after).

3rd law calculations

Instead of retaining the enthalpies using 2nd law of Norman et al [23] which may be inaccurate due to the small temperature range of measurements and a possible evolution of evaporation coefficients during the experiments (non-equilibrium state in their cells) two possibilities have been taken into account:

- (i) either calculate the original $I_i^+ \cdot T$ (proportional to the partial pressure) from the published figure 4 of Norman et al [23]
- (ii) or re-evaluate the sensitivity of the mass spectrometer with respect to the standard pressure of Ru(g) and then obtain the equilibrium constants to perform 3rd law calculations.

The measurement of $I_i^+ \cdot T$ products is related to partial pressures through the sensitivity of the mass spectrometer. Therefore, it is possible to relate the ion intensities of Ru⁺ (figure 4 of Norman et al [23]) to the pressure of Ru(g) over the pure element Ru(s) knowing that the vaporization of this component is at equilibrium. Indeed, Ru(g) has no reason to have an evaporation coefficient as shown by Pound [36] when compiling the pure components. As Norman et al [23] use this pressure of Ru(g) to calibrate their mass spectrometer - combined with the maximum ionization cross-sections (at 75 V) estimated by Otvos and Stevenson [30] – we make the same calculation using more recent estimates of the ionization cross-sections by Drowart et al [37] which allow the evaluation of the ionization cross sections at any ionization voltage.

First, the sensitivity S_{Ru} of the spectrometer is calculated with the basic spectrometric relationship using the pure Ru pressure,

$$S_{Ru} = \frac{I_{Ru}^+ T}{p_{Ru}} . \quad (43)$$

Thus, for Ru-oxides, an estimate of sensitivity ratios can be made based on the relationships,

$$\frac{S_{RuO}}{S_{Ru}} = \frac{\sigma_{RuO}}{\sigma_{Ru}} \sqrt{\frac{M_{Ru}}{M_{RuO}}} = 0.65 \times 0.93 \sim 0.6 \quad (44)$$

$$\frac{S_{RuO_2}}{S_{Ru}} = \frac{\sigma_{RuO_2}}{\sigma_{Ru}} \sqrt{\frac{M_{Ru}}{M_{RuO_2}}} = 0.77 \times 0.87 \sim 0.67 \quad (45)$$

where the ionization cross-section ratios are taken from the compilation of Drowart et al [37] (in their part 3.4) for oxides of the types MO(g) and MO₂(g) with respect to M(g) metal. The roots of the molar masses come from the type of detector as mentioned by Norman et al [23]. The ionization cross-section **ratios** mentioned in these relationships were established by cross-referencing numerous studies on gaseous oxides **for** low ionization potentials. For the RuO/Ru ionization cross sections ratio we use the above relation (44) since both ions are measured at the same low ionization potential 10 V.

For the ratio of RuO₂/Ru ionization cross-sections, as the RuO₂⁺ ion is measured at 20 V and the Ru⁺ ion at 10 V respectively - in fact to avoid contributions of any fragment ions in the ionic intensity evaluation - we estimate directly from the calculated ionization efficiency curves using Drowart et al [37] reference data (reported in Figure 2),

$$\frac{S_{RuO_2}}{S_{Ru}} = \frac{\sigma_{RuO_2}}{\sigma_{Ru}} \sqrt{\frac{M_{Ru}}{M_{RuO_2}}} = 2.96 \times 0.87 \sim 2.57 . \quad (46)$$

This more accurate estimate differs markedly from the proposed relationship as given in (45).

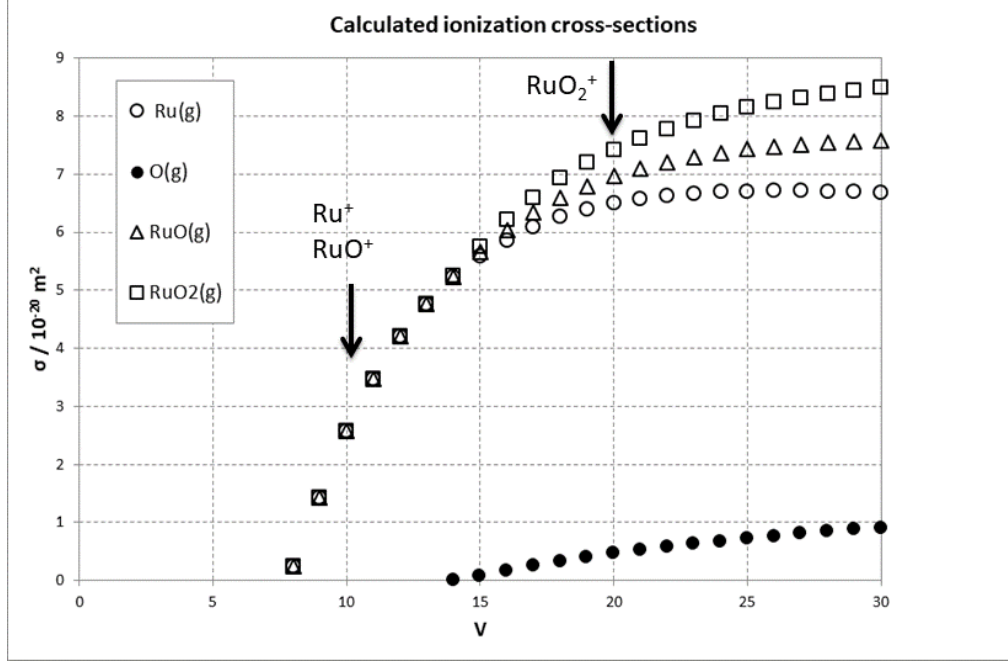


Figure 2: Ionization efficiency curves from Mann calculations and the additivity rule, according to Drowart et al [37]

Using the products $I_i^+ \cdot T^n$ from Figure 4 of Norman et al [23], they are converted into pressure-proportional products $I_i^+ \cdot T$ by the spectrometry relationship:

$$p_{\text{RuO}} = \frac{I_{\text{RuO}^+} \cdot T}{S_{\text{RuO}}} \quad (47)$$

$$p_{\text{RuO}_2} = \frac{I_{\text{RuO}_2^+} \cdot T}{S_{\text{RuO}_2}} \quad (48)$$

and normalized in pressure via their sensitivity,

$$\log(p_{\text{RuO}}) = \log(I_{\text{RuO}^+} \cdot T^{3/4}) + \frac{1}{4} \log T + \log S_{\text{RuO}} \quad (49)$$

$$\log(p_{\text{RuO}_2}) = \log(I_{\text{RuO}_2^+} \cdot T^{1/2}) + \frac{1}{2} \log T + \log S_{\text{RuO}_2} \quad (50)$$

First, sensitivity of Ru is calculated directly from the products $I_i^+ \cdot T$ derived from Figure 4 of Norman et al [23] and from the standard pressure of Ru(g) - in equilibrium with the pure Ru(s) - from Cordfunke and Konings [4] compilation. The standard enthalpy of sublimation of Ru(s) proposed by these authors [4] is $649 \pm 3 \text{ kJ mol}^{-1}$ - in agreement with the Hultgren [38] compilation (*i.e.* $651.4 \pm 4.2 \text{ kJ mol}^{-1}$). Indeed, this value is not so different from the 2nd law value proposed by Norman et al [23] and recalculated at 298K *i.e.* $639 + 8 = 647 \text{ kJ mol}^{-1}$. This agreement confirms that the vaporization of Ru(g) occurs at equilibrium in the experiment.

Then, partial pressures for RuO₂(g) and RuO(g) are re-calculated with our mass spectrometric sensitivity estimates and we perform 2nd and 3rd law calculations (Table 9). In 3rd law calculations, partial pressure of O₂ (g) molecule which enters into equilibrium constant determination is fixed in the range 10⁻³ to 10⁻⁵ bar to check the influence of the uncertainty of the pressure of O₂(g) that is not determined but only estimated at 10⁻⁴ bar by Norman et al [23]. Comparison of the 2nd and 3rd laws (table 9) values shows that some agreement could exist for RuO₂(g) molecule when increasing slightly the oxygen pressure but this is not possible for RuO(g). Moreover, trends in 3rd law results observed as a function of temperature let us assume some systematic errors in the determinations of equilibrium constants *i.e.* presence of some low evaporation coefficients (see Appendix II).

Table 9. 2nd and 3rd law calculations from partial pressure data of Norman et al [23] as corrected in this work from our estimates of ionization cross sections and sensitivity calibration with pure Ru(g) pressure.

Studied reaction (formation reaction)	2 nd law (T _{mean}) / kJ mol ⁻¹	2 nd law (298K) / kJ mol ⁻¹	3 rd law (298K) ± Standard deviation / kJ mol ⁻¹		
			10 ⁻³ /bar	10 ⁻⁴ / bar*	10 ⁻⁵ / bar
Oxygen pressure in cell	10 ⁻⁴ (est.) or constant /bar	10 ⁻⁴ (est.) or constant /bar			
Ru(s) + O ₂ (g) = RuO ₂ (g)	118.8	139.4	165.2 ± 1.3	129.1 ± 1.4	93.1 ± 3.2
Ru(s) + 1/2 O ₂ (g) = RuO(g)	355.6	379.7	354.9 ± 9.3	336.8 ± 8.3	318.8 ± 7.2

*this oxygen pressure value is the one estimated by Norman et al [23].

The values of 2nd law may be uncertain because of the small temperature range and the high sensitivity to any slight variation in the evaporation coefficients with temperature. Consequences of low evaporation coefficients as an indicator of non-equilibrium state in the cells are of two kinds:

- The flow of incident oxygen on the surface of Ru sample in the cells provides through a condensation coefficient a decrease of the effective oxygen partial pressure applied to the sample in the cells: the impact of such oxygen lower pressures can be evaluated when looking at the results in Table 9: decreasing the effective oxygen pressure let decrease the deduced enthalpies.
- The existence of evaporation coefficients associated to RuO(g) and RuO₂(g) species – leading to lower measured partial pressures than equilibrium one – is for instance to increase the third law deduced enthalpies by 38 kJ compared to equilibrium value (at a mean experimental temperature = 2000K) when the partial pressures in the Knudsen cell decrease by a factor 10, a value that can be achieved (see Appendix II).

The influence of evaporation and condensation coefficients is thus contradictory since equilibrium constants are based on partial pressure ratios versus oxygen pressures. To verify the

3rd law impact due to non-equilibrium state in the Knudsen cells, the above deduced 3rd law (formation) enthalpies must be compared to the maximum binding energies calculated with Born-Haber cycles from the ionization processes although these values are known with quite large uncertainties.

For the RuO₂(g) molecule, the dissociation energy associated with the Ru-O₂ bond (Table 8) leads to the enthalpy of formation:

$$\begin{aligned}\Delta_f H^\circ(\text{RuO}_2, g, 298\text{ K}) \\ = \Delta_f H^\circ(\text{Ru}, g, 298\text{ K}) - \Delta_{\text{diss.ionization}} H^\circ(\text{Ru} - \text{O}_2, g, 298\text{ K}).\end{aligned}\quad (51)$$

with the enthalpy of formation of Ru(g) from Cordfunke and Konings [4] (*i.e.* 649 ± 3 kJ mol⁻¹), and the dissociation energy from Table 8 (column 3), it becomes:

$$\Delta_f H^\circ(\text{RuO}_2, g, 298\text{ K}) = 649 - (\leq 490.6) = \geq 158.4 \pm 20\text{ kJ mol}^{-1}\quad (52)$$

This value could agree with that obtained by mass spectrometry *i.e.* 129.1 3rd law (Table 9) at the limit of uncertainty ranges for oxygen pressures around 10⁻⁴ bar, as estimated by Norman et al [23]. Besides, observed difference can have two origins:

- The experimental 3rd law value becomes more compatible with the Born-Haber cycle value if the oxygen pressure is largely higher than estimated in the mass spectrometric experiment but this oxygen increase would be contrary to the probable existence of an oxygen condensation coefficient
- The experimental 3rd law value increases for lower RuO₂(g) measured pressure values than equilibrium due to kinetic limitation (evaporation coefficient < 1): for a partial pressure decreasing by a factor 10, the experimental deduced enthalpy value 129.1 would result from an already increase of the equilibrium value by +38 kJ mol⁻¹ (see *Appendix III*) leading to an equilibrium enthalpy far from the 158.4 Born-Haber limit value.

The 3rd law enthalpies calculated using our new calibration remains anomalously low compared to the limit deduced from the Born-Haber cycle and all the more so since any partial pressures deficit due to kinetic limitation should increase this 3rd law value. Thus, we prefer to retain the value deduced from Born-Haber cycles which is really a low limit value:

$$\Delta_f H^\circ(\text{RuO}_2, g, 298\text{ K}) = 158 \pm 20\text{ kJ mol}^{-1}.\quad (55)$$

For the process associated with the breaking of the RuO-O bond (table 12) and with the above selected value for RuO₂(g) one obtains:

$$\begin{aligned}\Delta_f H^\circ(\text{RuO}, g, 298\text{ K}) \\ = \Delta_{\text{diss.ion}} H^\circ(\text{RuO} - \text{O}, g, 298\text{ K}) - \Delta_f H^\circ(\text{O}, g, 298\text{ K}) \\ + \Delta_f H^\circ(\text{RuO}_2, g, 298\text{ K})\end{aligned}\quad (56)$$

$$\Delta_f H^\circ(\text{RuO}, g, 298 \text{ K}) = (\leq 391.5) - 249.17 + (\geq 158.4) \\ \cong 300.7 \pm 28.3 \text{ kJ mol}^{-1}. \quad (57)$$

This last value could agree with the 3rd law formation enthalpy obtained by mass spectrometry (Table 9) due to compensation in kinetic energies of the two dissociative ionization processes that make varying the value of the term 300.7 up and down. The 3rd law value 336.8 is a mean value for experimental data that increase from 325 to 350 (see Appendix III) providing that measured partial pressures are lower than equilibrium ones due to low evaporation coefficient. Consequently, 3rd law enthalpy is over-evaluated (see Appendix III) and the Born-Haber cycle data is preferably retained:

$$\Delta_f H^\circ(\text{RuO}, g, 298 \text{ K}) = 301 \pm 28 \text{ kJ mol}^{-1}. \quad (58)$$

3 Conclusion

The thermodynamic assessment based on recalculations of the 3rd law carried out in this study allows us to propose a set of formation enthalpy values optimized for ruthenium gaseous oxides with the most probable uncertainties (Table 10). We observed that ab-initio calculations are in agreement with our recalculated value for RuO₃(g) and RuO₂(g) while differ from the present value proposed for RuO(g).

Table 10 Standard formation enthalpies issued from the present assessment compared to the preceding studies.

Compound	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$				
	This work	Cordfunke and Konings [4]	Miradji et al [7] Ab-initio	SGPS-SGTE [32]	TDNucl[33]
RuO ₂ (s)	-312.3 ± 0.6 [2]	-314.2 ± 0.5	-	-305.014	-314.199
RuO ₄ (g)	-197.6 ± 5.5	-188.0 ± 4	-188.0 ± 4*	-184.096	-183.091
RuO ₃ (g)	-53.0 ± 10	-62.5 ± 2.5	-50	-78.241	-78.240
RuO ₂ (g)	158 ± 20	136 ± 10	140	136.000	135.999
RuO (g)	301 ± 28	376 ± 25	420	375.999	376.000
Ru(g)	649 ± 3 [4]	649 ± 3	639	657.950	657.950

*Value of Cordfunke and Konings [4] used as a reference.

In order to improve the thermodynamic knowledge of the gaseous phase of Ru-O a number of questions remain to be answered:

- determinations of the total pressure on two-phase Ru(s)-RuO₂(s) systematically give higher values than direct measurements of the electromotive force (E.M.F.): in the previous work [2] we chose to select the E.M.F. data because they are all consistent when using very different electrochemical devices and reactions chains, which eliminates the possibility of systematic experimental errors. In the total vapor pressure measurement methods as the static method

(manometry at cold walls), the total pressure measurement is a measure of the total pressure of the non-condensable species $\text{O}_2(\text{g})$ at walls that is in mechanical equilibrium (given the pressure range > 1 mbar) with the sum of the pressures at the sample temperature. Condensable vapors are deposited in an intermediate location close to the hot sample, probably not very spread out because in the vapor phases only a very small temperature gradient is necessary to start condensation (of the order of a few degrees). There is then a stationary equilibrium of the diffusion flow between the sample and the nearest condensation site, which ensures a certain back flow of the vapors to the sample. Condensable vapors – mainly $\text{RuO}_4(\text{g})$ and $\text{RuO}_3(\text{g})$ – may be the cause of these higher total measured pressures. However, by performing thermodynamic calculations with the current selected data, one obtains the only percentage contribution of these molecules to the total pressure. This is not sufficient to explain the differences between the total pressures and the E.M.F. data.

- b) Enthalpy of formation of $\text{RuO}_2(\text{s})$ oxide by calorimetry must be accurately determined. Two calorimetric methods can be used - (i) either, by combustion and post-combustion with a more precise analysis of the residue to verify complete combustion, - (ii) or by dissolution techniques which can be more precise when choosing the appropriate chemical bath.
- c) Low pressure mass spectrometry determinations with a conventional effusion cell should confirm the presence of $\text{RuO}_4(\text{g})$ and $\text{RuO}_3(\text{g})$ in the vapor phase of $\text{RuO}_2(\text{s})$. However, different tests should be performed with different effusion orifices to control the equilibrium conditions in the cells avoiding any influence of evaporation coefficients on the measured pressures.
- d) Vapor pressure data for the sub-oxides $\text{RuO}(\text{g})$ and $\text{RuO}_2(\text{g})$ can only be obtained by mass spectrometric method when introducing small amounts of oxygen on pure $\text{Ru}(\text{s})$ in a Knudsen cell. However, equilibrium conditions have to be checked using different cells geometries and for a wide range of input oxygen pressure. A special oxygen flow device associated with an accurate flow calibration of the mass spectrometer could lead to larger range for observed oxygen pressures and at the same time a larger temperature range for the experiments.

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4 Appendix I. Literature compilation for molecular parameters for Ru-O gaseous molecules.

Table I-1. Literature Interatomic distances in different $RuO_n(g)$ ($n=1$ to 4) gaseous molecules

Authors	d (Ru-O ₄) / Å	d (Ru-O ₃) / Å	d (Ru-O ₂) / Å	d (Ru-O) / Å	Method
Hameka et al.[5]	1.6083	1.6098	1.5958		Effective Core Potential calculations
Siegbahn [6]	1.67	1.68	1.67		ab-initio calculations
Miradji et al [7]	1.691	1.687	1.685	1.713	ab-initio calculations
Zhou et al [8]			1.697		DFT calculations
Krauss et Stevens [9]				1.741	MC-SCF calculations
Schäfer et al. [10]*	1.7058				Gas electron diffraction
Pley and Wickleder [11]					XRD (solid)
Scullman and Thelin [12]	1.695 – 1.701			1.716	Band Spectroscopy

*Experimental diffraction on give s inter atomic distances

nces at mean temperature $\approx 1200K$. Other methods give theoretical values at 0 K.

Table I-2. Molecular parameters of $RuO_4(g)$

Authors	Method	Symmetry group	Electronic State / cm^{-1}	r_{Ru-O} / Å	Bond angles /°	ν_1 (1) / cm^{-1}	ν_2 (2) / cm^{-1}	ν_3 (3) / cm^{-1}	ν_4 (3) / cm^{-1}	Comments
Braune and Stute (1938)[14]	Electron diffraction	Regular tetrahedral T_d ($\sigma=12$)		1.66				920.8		
Dodd (1959)[17]	IR spectroscopy	Regular tetrahedral		2.23 calc.		880 calc		920		

		T _d				ulated				
<i>Ortner (1961)[18]</i>	Adsorption Spectra 650-5000 300-500 cm ⁻¹	T _d				880	293	913	330	
<i>Schäfer (1967) [10]</i>	Electron diffraction	T _d		1.7058 ± 0.003						Vibration amplitudes agree with spectroscopic results
<i>McDowell et al. (1972)[15]</i>	IR and Raman spectra with ¹⁸ O / ¹⁶ O isotopes	T _d		1.706 est. from Schäfer[10]		885.3	319	921	336	Vapor, Liquid and RuO ₄ dissolved in CCl ₄ v ₃ band contour analysis
<i>Königer and Müller (1977)[19]</i>	IR spectroscopy Matrix isolation. ¹⁰⁴ Ru/ ⁹⁹ Ru isotopes			1.706 est. from Schäfer[10]				919.2 Ar 923.4 vapor		vapor phase v ₃ band contour analysis
<i>Kay et al. (1989)[16]</i>	FTIR spectroscopy with ¹⁸ O / ¹⁶ O in Ar Matrix	T _d						920.8		
<i>Green et al. (1989)[13]</i>	FTIR Matrix Isolation in	T _d Undistorted				882.5		916.9 obs.		From Vapor

	Ar. ^{16}O - ^{18}O isotopes	d Confirmed by FG matrix calculations				calc.		915.9 calc.		RuO_4
<i>Hameka et al.</i> (1991)[5]	Effective Core Potential calculations Vibration frequencies	T_d		1.6083		1055	398	923	413	Use of effective core potentials in “Gaussian 90 Prog. Pack. “
<i>Siegbahn</i> (1993)[6]	ab-initio calculations	T_d	1A_1	1.67						Influence of 4d orbitals filling as a function of the number of O
<i>Zhou et al.</i> (2000)[8]	Ru Laser ablation under O_2 Trap in Ar or Ne matrix. IR spectra and DFT calculations	T_d						916.9 (Ar) 923 (Ne) 950.2		
<i>Pley and Wickleder,</i> (2005)[11]	XRD on condensed RuO_4 solids from KReO_4 vaporization	Cubic symmetry $P4$ group Monoclini c		1.695 1.697- 1.701	109.3 108.9 – 110.1					Basic tetrahedron RuO_4 Very small deformation

		symmetry C2 group								
<i>F. Miradji et al. (2015) [7]</i>	Ab-initio Calculations TPSSh-5%HF	T _d	¹ A ₁ and Triplet state at 170 kJ mol ⁻¹ = 14210 cm ⁻¹	1.691		952	327	974.3	350	
<i>This work</i>	Selected	T_d	g₀=1 ε₀=0 g₁=3 ε₁=14210	1.7058 ± 0.003 From Schäfer [10] E.D. Slightly more than DRX on solids	109.471° Undistorted tetrahedral from Greene et al[13]	885.3 Meas. by Mc Dowell [15] Matrix Isolation	319 Meas. by Mc Dowell [15] Matrix Isolation	921 Meas. by Mc Dowell [15] Matrix Isolation	336 Meas. by Mc Dowell [15] Matrix Isolation	Selection based on main experimental features Electronic structure as calculated by quantum chemistry
				I_AI_BI_C*/cgs = 8.75900 · 10⁻¹¹⁴		Matrix Isolation				

* I_AI_BI_C calculated using the selected values for interatomic distances and bond angle

Table I-3. Molecular parameters of RuO₃(g)

Authors	Method	Symmetry Group	Elec. State / cm ⁻¹	r _{Ru-O} / Å	Bond angles	v ₁ (1) / cm ⁻¹	v ₂ (2) / cm ⁻¹	v ₃ (2) / cm ⁻¹	v ₄ (1) / cm ⁻¹	Comments
<i>Kay et al. (1989)[16]</i>	FTIR spectroscopy with ¹⁸ O / ¹⁶ O in Ar Matrix Isolation	D _{3h} (assumed planar) σ = 6			120°	950.1 (1) (estimated)		893.4 (2)		Calculated force constants High resolution due to isotopes

<i>Hameka et al. (1991)[5]</i>	Effective Core Potential calculations Vibration frequencies	D _{3h}		1.6098	120°	1054.9(1)	329.8(2)	758.6(2)	185.0(1)	
<i>Siegbahn (1993)[6]</i>	ab-initio calculations	D _{3h}	¹ A ₁	1.68						Influence of 4d orbitals filling as function of the oxygen number
<i>Zhou et al. (2000)[8]</i>	Ru Laser ablation under O ₂ Trapping in Ar or Ne matrix. IR spectra and DFT calculations	C _{3v} deduced from anti-symmetric v ₃ D _{3h}	¹ A ₁					954.0 and 953.4 974.9		Vibrations deduced from C _{3v} structure assumption
<i>F. Miradji et al. (2015)[7]</i>	Ab-initio Calculations TPSSh-5%HF	D _{3h}	¹ A ₁ and Triplet state at 62 kJ mol ⁻¹ = 5183 cm ⁻¹	1.687	120°	963.9	298.2	963	71.3	
<i>This work</i>	Selected	D_{3h} σ = 6	g₀=1 ε₀=0 g₁=3 ε₁= 5183	1.7058 ± 0.003 As RuO4	120°	950.1	298.2	893.4	71.3	Retained Frequencies from Kay et al[16] and Miradji et al[7]
				I _A I _B I _C */cgs						

				$=3.11783 \cdot 10^{-114}$					
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* $I_A I_B I_C$ calculated using the selected values for interatomic distances and bond angle

Table I- 4. Molecular parameters of $RuO_2(g)$

Authors	Method	Symmetry Group (σ)	Electronic State / cm^{-1}	r_{Ru-O} / Å	Angle / °	$\nu_1 (1)$ / cm^{-1}	$\nu_2 (1)$ / cm^{-1}	$\nu_3 (1)$ / cm^{-1}	Comments
Kay et al. (1989)[16]	FTIR spectroscopy with $^{18}O/^{16}O$ in Ar Matrix Isolation	C_{2v} $\sigma = 2$			$149 \pm 2^\circ$	926		902.2	Full isotopic resolution Calculated force constants
Hameka et al. (1991)[5]	Effective Core Potential calculations Vibration frequencies	C_{2v}	Close singlet states Triplet at 42.4 kJ mol^{-1} $=3547 \text{ cm}^{-1}$	1.5953	150.6°	1098.2	308.6	817.2	
Siegbahn (1993)[6]	ab-initio calculations	C_{2v}	1A_1	1.67	152.8°				Influence of 4d orbitals filling as a function of the number of Oxygen
Zhou et al. (2000) [8]	Ru Laser ablation under O_2 and trapping in Ar or Ne matrix. IR spectra and 2 DFT calculations	C_{2v} C_{2v}	 1A_1	 1.697	$150 \pm 1^\circ$ Ne $150.1^\circ - 152.4^\circ$	924.7 (^{102}Ru) $947.8 - 964.8$ (^{102}Ru)		876.5 Ne (^{102}Ru) $989.7 - 990.1$ (^{102}Ru)	Symmetric and anti-symmetric vibrations are not in agreement between experiment and DFT calc.

<i>F. Miradji et al. (2015)[7]</i>	Ab-initio Calculations TPSSh-5%HF	C_{2v}	1A_1 Lowest triplet state at $4 \text{ kJ mol}^{-1} = 334 \text{ cm}^{-1}$	1.685	149.8°	972.4	191.7	964.4	
<i>This work</i>	Selection	C_{2v} $\sigma=2$	$g_0=1$ $\epsilon_0=0$ $g_1=3$ $\epsilon_1 = 334 \text{ cm}^{-1}$	1.7058 Same distance as in RuO_4	149.8°	926	180	902.2	ν_2 frequency scaled to ν_1 and ν_3 between Miradji et al[7] and experimental values of Kay et al[16]
				$I_A I_B I_C^*/\text{cgs} = 1.62249$					

* $I_A I_B I_C$ calculated using the selected values for interatomic distances and bond angle

Table I-5. Molecular parameters of RuO (g)

Authors	Experimental Methods	Electronic States $\epsilon_i / \text{cm}^{-1}$	$r_{\text{Ru-O}} / \text{\AA}$	$\omega_e / \text{cm}^{-1}$	$\omega_e x_e / \text{cm}^{-1}$	B_e / cm^{-1}	$\alpha_e / \text{cm}^{-1}$	D_e / cm^{-1}	Comments
<i>Raziunas et al. (1965)[20]</i>	Atomic Emission Spectroscopy Band system analysis	$^3\Sigma^+$ $g_0=3$ $\epsilon_0=0$ $^3\Sigma^+ \rightarrow X$ at 18876.1	1.70	880.8	13.1	0.422			
<i>Scullman and Thelin (1975)[12]</i>	Atomic Emission Spectroscopy (5000 to 6800 \AA) Band system analysis	Transition around 17000-18000	1.716	863.5	4.6	0.4137	0.0028	0.3	Refined analysis compared to preceding one from Raziunas et al. [20]

<i>Krauss and Stevens (1985)[9]</i>	Quantum chemistry MC-SCF with Relativistic Effective Potentials.	$^5\Delta$ $g_0=10$ $\epsilon_0=0$	1.741	814	5.0				
<i>Kay et al. (1989)[16]</i>	FTIR spectroscopy with $^{18}\text{O}/^{16}\text{O}$ in Ar Matrix			839	1.8				Full isotopic resolution Force constants calculated
<i>Zhou et al. (2000) [8]</i>	Ru Laser ablation and co-deposition with O_2 in Ar or Ne matrix. IR spectra and DFT calculations	$^5\Delta$		834.2 (Ar) 849.7 (Ne) 859.9 - 862.7					
<i>F. Miradji et al. (2015) [7]</i>	Ab-initio Six different calculations	$^5\Delta$	1.709 – 1.721 1.713 retained	895 retained					
<i>Gaydon (1968)[21]</i>	Compiled from <i>Raziunas et al. (1965) [20]</i>								$D^\circ_0 = 175.7 \pm 1.7 \text{ kJ mol}^{-1}$
<i>Hüber and Hertzberg (1995)[22]</i>	Compilation from <i>Scullman and Thelin (1975) [12]</i>	A_1 Obs. Transition at $g_1=1$ $\epsilon_1=18024$	1.716(8)	863.5	4.6	0.4137	0.0028	3	$D^\circ_0 = 511.3 \text{ kJ mol}^{-1}$ from <i>Norman et al (1968) [23]</i>
<i>This work</i>	Our selection ^a	$g_0=3$ $\epsilon_0=0$ $g_1=3$ $\epsilon_1=17500$	1.716	863.5	4.6	0.4137*	0.0028	0.3	Exp ^{al} values from Raziunas et al [20] and Scullman and Thelin[12]

5 Appendix II. Vapor pressures and evaporation coefficients.

Evaporation coefficients were originally defined by comparing under vacuum the free vaporization flows F_i of a surface with those calculated or measured at equilibrium with an effusion cell. The evaporation coefficient α for a gaseous species i is defined as follows either from molecular flows F or from measured pressures p ,

$$\alpha_i = \frac{F_i^{free}}{F_i^{eq}} = \frac{p_i^{free}}{p_i^{eq}} \quad (\text{II-1})$$

per unit of surface (free surface or cross-section of the effusion orifice). Coefficients values $\alpha_i = 1$ are for equilibrium conditions and $\alpha_i < 1$ are for any surface vaporizing with a kinetic barrier. Any low evaporation coefficient existing at the sample surface in an effusion cell will causes any pressure drop. Thus, pressures measured with the Knudsen cell method by mass spectrometry can be schematically represented in Figure II-1. The evaporation coefficients may be constant as a function of the inverse of temperature or may show a logarithmic variation similar to Arrhenius law -. Therefore, a vapor pressure determined by effusion method leads either to a curve parallel to the equilibrium curve or to a curve reaching equilibrium values at high temperature. Experimental pressure parallel to equilibrium pressure corresponds to any entropy barrier associated with the kinetics of species formation in the adsorbed layer before evaporation (frequency factor in the Arrhenius law) while a non-parallel line reflects two combined effects - enthalpy barrier (activation) and entropy barrier.

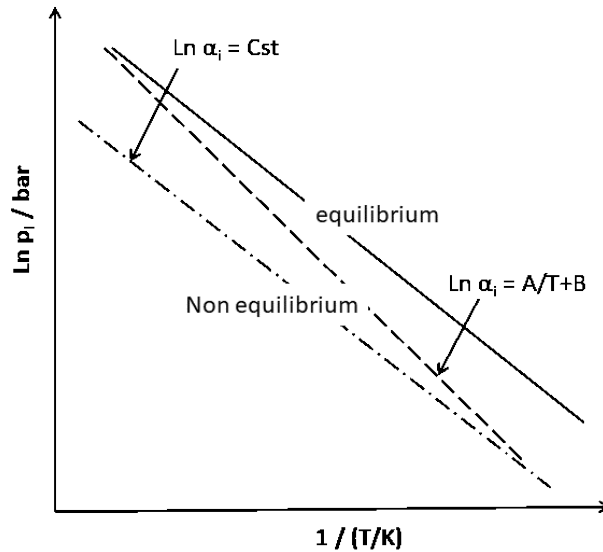


Figure II-1. Effect of the presence of a kinetic limitation in the vaporization reactions at the surface of the sample - presence of an evaporation coefficient α_i - on the partial pressures measured by effusion mass spectrometry.

For $\text{RuO}_3(\text{g})$ molecule, the 2nd law enthalpy of reaction (4) proposed by Norman et al. [23] is quite close to original determinations of Schäfer et al [26] and Bell and Tagami [27], whereas the entropy obtained in their publication after spectrometer calibration is clearly different from that calculated from our selection. We can conclude that an evaporation coefficient is associated with this molecule, and that it is a constant value as a function of temperature due to similar enthalpy values (similar slopes). Under these conditions, the calculations of the 3rd law that we have made from the Gibbs energy data of Norman et al [23] lead to trends in standard enthalpies as a function of temperature.

Assuming constant evaporation coefficients, the value of the pressure difference measured in the effusion cell relative to the equilibrium pressure can be deduced from the following two relationships applied to their vaporization reactions:

(i) at equilibrium with the thermodynamic functions (standard °):

$$-RT \ln p_{eq} = \Delta_r H_T^\circ - T \Delta_r S_T^\circ \quad (\text{II-2})$$

(ii) for the measurements in non-equilibrium with a kinetic limitation (*):

$$-RT \ln p_{meas} = RT \ln \beta p_{eq} = \Delta_r H_T^* - T \Delta_r S_T^* \quad (\text{II-3})$$

The β coefficient reflects the pressure deficit in the cell ($\beta \leq 1$) due to α evaporation coefficient at the sample surface ($\alpha \leq 1$). The relationship between the two coefficients α and β is generally deduced from the Motzfeldt's relationship [39] (see also Heyrman et al [40]) who established it by considering the steady-state flows in effusion cells. In the present case, the effusion pressure deficit - coefficient β - can be evaluated from the entropies calculated at equilibrium with respect to the experimental entropies published by Norman et al [23] in their page 107,

$$\ln \beta = \frac{\Delta_r S_T^* - \Delta_r S_T^\circ}{R} \quad (\text{II-4})$$

which gives the following values in table II-1 for the different species.

Table II-1. Partial pressure ratio (β = measured pressure / equilibrium pressure) for $\text{RuO}_3(\text{g})$, $\text{RuO}_2(\text{g})$, $\text{RuO}(\text{g})$ and estimated evaporation coefficient α .

	$\text{RuO}_3(\text{g})$	$\text{RuO}_2(\text{g})$	$\text{RuO}(\text{g})$
$\ln \beta$	-3.586	-3, .210	-4.706
β	0.028	0.040	0.009
α	$2.8 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$\approx 10^{-4}$

Using the reactions entropies, the β coefficients are effectively < 1 , which surely reflects a kinetic limitation of the vaporization reactions. Applying the Motzfeldt's relation for an arbitrarily ortho-cylindrical effusion cell that relates the theoretical equilibrium pressure to the measured pressure,

$$p_{eq} = p_{meas} \left(1 + \frac{f}{\alpha}\right) \quad (\text{II-5})$$

and with a usual ratio $f = sC/S = 10^{-2}$ (s is the area of orifice and C the Clausing coefficient of the effusion orifice, S the cross section of the cell) we obtain a value of the evaporation coefficient α mentioned in the last row of Table II-1. These coefficients are very low and unlikely at least for $\text{RuO}(\text{g})$ which does not really require significant surface rearrangement in the adsorbed layer. There is probably – (i) in the value of the coefficient β some uncertainty in the spectrometer pressure calibration procedure, and – (ii) in the equilibrium constants an uncertainty in the applied pressure of $\text{O}_2(\text{g})$ since the authors estimated it to be about 10^{-4} bar but did not calibrate it. Moreover, the $\text{O}_2(\text{g})$ molecule when it arrives at the surface of Ru must dissociate to form an adsorbed O_{ads} species and the reaction can be limited kinetically (the so-called condensation coefficient < 1). Insufficient O_{ads} adsorption concentration at the surface is equivalent to an oxygen potential deficit at the surface of Ru in the Knudsen cell sample. At this point, the production of gaseous oxides is reduced and contributes to the decrease of partial pressures compared to those expected at equilibrium. Therefore, a part of the value of the coefficient β is explained in this way.

6 Appendix III. 3rd law calculations with Norman et al [23] original data

Starting from $\Delta_r H^\circ(T)$ and $\Delta_r S^\circ(T)$ proposed by Norman et al [23] as issued from 2nd law we calculate the function $\Delta_r G^\circ(T)$ for arbitrarily different temperature increments in their available temperature range and consequently the equilibrium constant is deduced:

$$\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T \cdot \Delta_r S^\circ(T) = -RT \ln K_p(T) \quad (\text{III-1})$$

From the equilibrium constant, 3rd law enthalpy values are calculated using our retained free energy functions

$$\Delta_r H^\circ(T) = -RT \ln K_p(T) + T \cdot \Delta_r F_{\text{ef}}^\circ(T) \quad (\text{III-2})$$

and presented in Table III-1. We observe a trend in the deduced 3rd law enthalpies as a function of temperature in place of a statistic distribution around a mean value. Consequently, one of the two terms of the 3rd law relationship is misjudged. Since our free energy functions are well known, it is likely that the equilibrium constants or partial pressures are poorly evaluated. Moreover, the enthalpies of the 2nd law of Norman et al. [23] corrected at 298 K using our selected thermal functions (enthalpy increments) largely disagree with the enthalpies values of the 3rd law.

Table III-1. 3rd law formation enthalpies at 298 K for ruthenium gaseous oxides obtained from the values of the equilibrium constants calculated according to enthalpies and entropies provided by Norman et al. [23] 2nd law treatment. The free energy functions are those compiled in this work.

$\text{Ru}(\text{s}) + 3/2 \text{O}_2(\text{g}) = \text{RuO}_3(\text{g})$			
T / K*	ln Kp	$\Delta_r F_{\text{ef}}^\circ(T) / \text{J K}^{-1}$	$\Delta_r H^\circ(298 \text{ K}) / \text{kJ}$ ± Standard deviation
1285	-3.810	-55.392	-30.476
1300	-3.886	-55.373	-29.978

1350	-4.130	-55.299	-28.294
1400	-4.356	-55.209	-26.582
1450	-4.567	-55.111	-24.850
1500	-4.764	-55.012	-23.105
1538	-4.905	-54.940	-21.777
Mean value \pm standard deviation			-26.4 \pm 3.4
2nd law at 298 K			-60.7 **
Ru(s) + O₂(g) = RuO₂(g)			
1740	-8.968	29.264	180.7
1800	-8.694	29.060	182.4
1850	-8.480	28.867	183.8
1900	-8.277	28.654	185.2
1850	-8.480	28.867	183.8
2000	-7.901	28.167	187.7
2040	-7.760	27.953	188.6
Mean value \pm standard deviation			184.6 \pm 2.8
2nd law at 298 K			139.4 \pm 4.2**
Ru(s) + 1/2 O₂(g) = RuO (g)			
1870	-16.936	98.311	447.2
1900	-16.574	98.153	448.3
1950	-15.997	97.891	450.3
2000	-15.449	97.630	452.2
2020	-15.237	97.527	452.9
Mean value \pm standard deviation			450.2 \pm 2.4
2nd law at 298 K			355.6 \pm 20.9**

*Temperatures are chosen arbitrarily but included in the temperature range of the experiment.

**Values and uncertainty listed according to Norman et al. [23]

Table III-2. 3rd law formation enthalpies at 298 K for ruthenium gaseous oxides obtained from new partial pressures calculated from Norman et al. [23] figures and our mass spectrometric calibration procedure. The free energy functions are those compiled in this work.

Ru(s) + O₂(g) = RuO₂(g)			
T / K*	ln Kp	$\Delta_r \text{Fef}(T) / \text{J K}^{-1}$	$\Delta_f \text{H}^\circ(298 \text{ K}) / \text{kJ}$ \pm Standard deviation
1736	-5.523	29.275	130.6
1782	-5.357	29.124	131.3
1843	-4.929	28.897	128.8
1884	-4.817	28.725	129.6
1926	-4.519	28.536	127.3
1976	-4.389	28.293	128.0
2038	-4.215	27.962	128.4
Mean value \pm standard deviation			129.1 \pm 1.4
2nd law at 298 K			134.2 \pm 4.2**
Ru(s) + 1/2 O₂(g) = RuO (g)			

1736	-10.601	99.295	325.5
1782	-10.278	99.082	328.9
1843	-9.942	98.784	334.3
1884	-9.712	98.570	337.8
1926	-9.334	98.345	338.8
1976	-9.068	98.065	342.7
2038	-8.897	97.698	349.9
Mean value \pm standard deviation			336.8 \pm 8.3
2nd law at 298 K			173.3 \pm 20.9**

*Temperatures are extracted from Norman et al [23] figures.

**Uncertainty listed according to Norman et al. [23].

Influence of a decrease of the RuO(g) and RuO₂(g) measured partial pressures compared to equilibrium pressures on the 3rd law enthalpies is evaluated as follow:

$$\Delta_r H^\circ(298K) = -RT \ln K_p(T) + T \cdot \Delta_r F_{ef}^\circ(T) \text{ for equilibrium} \quad (\text{III-3})$$

$$\Delta_r H^*(298K) = -RT \ln K^*(T) + T \cdot \Delta_r F_{ef}^\circ(T) \text{ as measured} \quad (\text{III-4})$$

and for the same free energy function value,

$$\begin{aligned} \Delta_r H^*(298K) &= \Delta_r H^\circ(298K) + RT \ln \frac{K^*(T)}{K_p(T)} \\ &= \Delta_r H^\circ(298K) + RT \ln \frac{p_{RuO_2(meas.)}}{p_{RuO_2(eq.)}} \end{aligned} \quad (\text{III-5})$$

For a pressure ratio ≈ 0.1 and a mean temperature of measurements = 2000 K,

$$\Delta_r H^*(298K) = \Delta_r H^\circ(298K) + 38 \text{ /kJ}. \quad (\text{III-6})$$

Note that the effect is reverse for oxygen pressures when a condensation coefficient occurs.

7 References

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