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Critical Evaluation and Calorimetric Study of the Thermodynamic Properties of Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 , and K_2WO_4

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Abstract: This paper evaluates crystallographic data and thermodynamic properties for sodium chromate (Na_2CrO_4), potassium chromate (K_2CrO_4), sodium molybdate (Na_2MoO_4), potassium molybdate (K_2MoO_4), sodium tungstate (Na_2WO_4), and potassium tungstate (K_2WO_4) collected from the literature. A thorough literature review was carried out to obtain a good understanding of the available data, and a critical evaluation has been performed from room temperature to above the melting temperatures. Also, the solid-solid transition and melting properties of the six pure salts were measured by differential scanning calorimetry (DSC), and high-temperature X-ray powder diffraction (XRD) measurements were performed to determine the crystal structures and space groups associated with the phases of K_2MoO_4 . This work is the first step towards the development of a thermodynamic model for the Na^+ , K^+ // Cl^- , SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$, O^{2-} system that is relevant for high temperature corrosion in atmospheres containing O-H-S-C-Cl and alkali salts.

Keywords: Thermodynamic properties; DSC; Alkali chromates; Alkali molybdates; Alkali tungstates; Crystal structures.

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1. Introduction

Combustion installations suffer from the problem of hot corrosion, which limits their efficiency. ¹⁻
⁴ This phenomenon is an accelerated form of oxidation (from 600 °C to 950 °C) ^{5, 6} affecting
equipment in the presence of high-temperature combustion gases (N₂, CO₂, CO, O₂, H₂O, etc.)
containing impurities (SO₂, Cl₂, S₂, HCl, etc.) and corrosive products (Na₂O, K₂O, NaOH, KOH,
NaCl, KCl, etc.). ^{3, 4, 7} The formation of ashes and corrosive gases is mainly due to the elements K,
Na, Ca, Mg, Fe, Al, Si, P, S, Cl, C, H, and O. ^{8, 9} Stainless steels containing the alloying elements
Ni, Cr, Mo, W, and V are particularly prone to this problem. ^{2, 4, 10-12} They are frequently exposed
to gaseous species generated during combustion (O₂, CO₂, SO₂, H₂O) or from the evaporation of
ashes (KCl, NaCl, Na₂SO₄, K₂SO₄, Na₂CO₃, K₂CO₃). ^{3, 4, 6, 13}

Oxides formed from these alloying elements, such as Cr₂O₃, ^{10, 14} MoO₃, WO₃, and V₂O₅, ^{1, 10, 12}
often react with the KCl, NaCl, Na₂SO₄, K₂SO₄, Na₂CO₃, and K₂CO₃ present during the operating
conditions of these installations and/or originating from the fuel used. Those along with the quantity
of air required for combustion contribute to the oxidation of the alloying elements. The literature
reports that, under operating conditions, corrosive deposits in the form of Na₂CrO₄ and K₂CrO₄ ^{14,}
¹⁵ may be formed on the walls of installations. Other salts can further enhance the corrosion,
particularly sodium molybdate, ^{15, 16} potassium molybdate, sodium tungstate, ^{15, 17} and potassium
tungstate. These may be present in solid or liquid form.

Studies by Misra ¹¹ and Fryberg ¹⁶ revealed the complete conversion of Na₂SO₄ to Na₂CrO₄ before
the onset of catastrophic corrosion for Mo-containing superalloys. Initiation of catastrophic
corrosion was characterized by the conversion of Na₂CrO₄ to Na₂MoO₄ observed in the MoO₃-rich
layer at the scale-metal interface, related to fluxing by the Na₂MoO₄-MoO₃ mixture.

Catastrophic corrosion is attributable to the formation of Na₂MoO₄ and a Na₂MoO₄-MoO₃ mixture,
but its mechanisms are still unclear. The presence of sodium in the MoO₃-WO₃ zones reduces the
melting temperature by forming Na₂MoO₄-Na₂WO₄. ¹⁶ Furthermore, Bourhis and Saint-John ¹⁸
reported catastrophic corrosion in Mo-containing superalloys related to fluxing by MoO₃, which
forms at the scale-metal interface.

In this context, predicting potential corrosion products to ensure the preservation of equipment while maximizing the rate of conversion into electrical energy is extremely important. Indeed, the various deposits, rich in salts, are generally very corrosive and, when present in liquid form, often dissolve the protective oxide layers and attack the metal surface.¹⁹

A thermodynamic model for the Na^+ , K^+ // Cl^- , SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$, O^{2-} system is being developed. This will permit us to make phase equilibrium calculations, and thus assess the limiting conditions under which deposits are susceptible to form and then prevent their formation. As a first step, it is necessary to investigate the crystal structures and thermodynamic properties (including solid-solid transitions and fusion) of all relevant pure salts. The present article is devoted to a thorough literature review for the sodium and potassium chromates, molybdates, and tungstates. The sodium and potassium dichromates, dimolybdates and ditungstates will be discussed in a subsequent paper. For the six compounds considered in this work, literature data are sometimes lacking or contradictory. Therefore, differential scanning calorimetry (DSC) was used to measure the temperature and enthalpy change for the solid-solid transitions and fusion of the various compounds investigated. In addition, high temperature X-ray diffraction (XRD) measurements were conducted for K_2MoO_4 .

2. Experimental procedure

2.1. DSC/TGA (differential scanning calorimetry/thermogravimetric analysis)

Materials and measurements

The initial reagents used in this study were 99.999 % pure Ar (gas) from Oy Linde Gas AB (Finland), $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$, K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and K_2WO_4 . The following Table presents the supplier's name, CAS number, and purity for each solid reagent.

Chemical formula	Supplier	CAS number	Purity (%)
$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$	Sigma-Aldrich	10034-82-9	99.0
K_2CrO_4	Alfa-Aesar	7789-00-6	99.9

Na ₂ MoO ₄	Sigma-Aldrich	7631-95-0	99.9
K ₂ MoO ₄	Sigma-Aldrich	13446-49-6	98
Na ₂ WO ₄ ·2H ₂ O	Sigma-Aldrich	10213-10-2	99.995
K ₂ WO ₄	Alfa-Aesar	7790-60-5	99.5

DSC/TGA (differential scanning calorimetry/thermogravimetric analysis) experiments were conducted to measure the temperature and enthalpy change for the solid-solid transitions and fusion of the pure compounds Na₂CrO₄, K₂CrO₄, Na₂MoO₄, K₂MoO₄, Na₂WO₄, and K₂WO₄. These measurements were performed using a NETZSCH STA 449 F1 Jupiter® simultaneous DSC-TGA equipment.

The calibration of the DSC apparatus was performed using the known enthalpy changes and transition temperatures of the following reference substances (ultra-pure salts):

BaCO₃ (purity of 99.98 %) with $T_{\text{trs}}(\text{I} \rightarrow \text{II}) = 808 \text{ }^\circ\text{C}$;

CsCl (purity of 99.99 %) with $T_{\text{trs}}(\text{I} \rightarrow \text{II}) = 476 \text{ }^\circ\text{C}$;

Ag₂SO₄ (purity of 99.999 %) with $T_{\text{trs}}(\text{I} \rightarrow \text{II}) = 426 \text{ }^\circ\text{C}$;

and C₆H₅COOH (purity of 99.5 %) with $T_{\text{trs}}(\text{sol} \rightarrow \text{L}) = 122 \text{ }^\circ\text{C}$.

Variations recorded during the calibration measurements were used to estimate the experimental error for the temperatures and enthalpy changes as $\pm 1 \text{ }^\circ\text{C}$ and $\pm 10 \text{ } \%$ minimum, respectively.

A dehydration treatment of all pure compounds was performed prior to the DSC measurements. This operation was performed in a Vulcan oven temperature (Model: 3-130) to eliminate water absorbed by the samples during their storage, and also most of the water present in the initial reagents Na₂CrO₄·4H₂O and Na₂WO₄·2H₂O. All reagents were heated for 3 hours at 200 °C and then cooled to 25 °C.

About 45 mg of the dehydrated samples were added in a Pt/Rh (80/20) crucible, and a flow rate of 70 ml/min of Ar was used as a protective gas in all runs.

Initial heating was performed from room temperature to 40 °C, followed by a 10 min isothermal hold to ensure thermal stability of the sample and reference. Three consecutive heating-cooling cycles were then conducted for each sample, with a heating/cooling rate of 10 °C/min.

The maximum temperature investigated was always 49 °C above the predetermined melting temperature of each compound while the minimum temperature investigated was at least 50 °C below the temperature of the first solid-solid transition, with a holding time of one minute in each case. The maximum temperature selected was low enough to avoid vaporization of the compound, but high enough to ensure complete fusion.

Thermogravimetric analysis (TGA) was conducted to monitor mass loss or volatilization. Mass loss and heat flux were both measured continuously throughout the DSC experiments. A maximum mass loss of -3 % was always targeted during the experiments. For each pure compound, the overall mass loss was monitored at the end of each DSC experiment: -1.08 % for Na₂CrO₄, -1.01 % for K₂CrO₄, -0.12 % for Na₂MoO₄, -0.1 % for K₂MoO₄, -0.02 % for Na₂WO₄, and -0.63 % for K₂WO₄.

Each solid-solid transition and melting temperature was defined as the temperature at the onset of the peak. The first heating/cooling cycle was always discarded owing to non-reproducible data (i.e. thermal history of the sample).

Setting up the baseline

The first requirement is to establish a baseline before making the actual measurement for a sample. This can be obtained from the signal recorded during a temperature cycle applied to two empty crucibles.

The difference between the baseline and the signal obtained, under the same experimental conditions (i.e. nature of crucibles, temperature profile, heating/cooling rate, and flow rate of gas), depends on the material whose thermal behavior is to be studied. It is essential to have a suitable baseline for each analysis program. Pt/Rh (80/20) crucibles with the same mass were used for the baseline (blank run), the sapphire holder, and the sample holder in all DSC-TGA experiments.

2.2. High temperature X-ray diffraction

XRD patterns for K₂MoO₄ were determined using a 98 % purity commercial sample in powder form purchased from Sigma-Aldrich, Germany.

The powder was ground in an agate mortar to ~50 μm particle size to ensure cohesion and then spread evenly on a flat sample holder. The used XRD device was X'Pert Pro MPD Powder model

(by Malvern Panalytical), which was connected to a high-temperature chamber Anton Paar HTK 1200N and temperature controller TCU1000N. This setup enabled autonomous temperature control and diffraction measurements. Tube gave CuK α radiation and was set at 40 kV and 40 mA.

The sample holder was equipped with an alumina ring as the sample crucible and Pt-10%Rh thermocouple (type-S) to provide good correspondence between actual and set temperatures. Measurements were carried out at 25 °C, 350 °C, 465 °C, and 500 °C, with a heating rate of 10 °C/min between set points. After the measurement at 500 °C, the sample was cooled to 25 °C and the measurement was repeated at this temperature to confirm the stability of the sample. Measurements were done in a normal air atmosphere and using a secondary monochromator. Measurement angles were from 10 to 70° for a total duration of 1 hour per temperature point. The sample was held at a temperature set point for 1 hour before being scanned so that it had time to react or change morphology.

3. Crystal structures and space groups

A critical review of the literature related to the crystal structures and space groups of the six pure compounds is provided in this section.

Crystal structure information for phases of Na₂CrO₄ and K₂CrO₄ is summarized in Tables 1 and 2, respectively.

Table 1 : Crystallographic data for phases of Na₂CrO₄

Phase	Crystal structure	T(°C)	Space group	Reference
Na ₂ CrO ₄ (I)	Orthorhombic	< 419	D _{2h} ⁶ -Pbnn	20
			Cmcm	21
				22
				23
				24
				25
Na ₂ CrO ₄ (II)	Hexagonal	419 to 793	P6 ₃ mc	23
			P6 ₃ /mmc	26

Table 2 : Crystallographic data for phases of K₂CrO₄

Phase	Crystal structure	T(°C)	Space group	Reference
K ₂ CrO ₄ (I)	Orthorhombic	< 669	Pcmn	23
			Pnam	27
			-	28
K ₂ CrO ₄ (II)	Hexagonal	669 to 976	P6 ₃ mc	23
			P6/mmc, P6mc, P6̄2c, P3̄1c, P31c	27

Miller's ²⁰ visual estimation in single-crystal X-ray oscillation intensities showed that Na₂CrO₄(I) (low-temperature phase) is orthorhombic with D_{2h}⁶-Pbnn space group. This study was subsequently reviewed by Fischmeister, ²¹ Niggli, ²² Goldberg, ²³ Nimmo, ²⁴ and Amirthalingam ²⁵ who confirmed a different space group, Cmcn.

The crystal structure of K₂CrO₄(I) at room temperature has been investigated by XRD. ^{23, 26, 27} An orthorhombic structure has been reported with space group Pnam ^{26, 27} or Pcmn. ²³

The high-temperature phases Na₂CrO₄(II) and K₂CrO₄(II) exhibit hexagonal structures. The analysis of high-temperature XRD diffractograms of A₂BX₄-type compounds suggests the space group P6₃mc for both phases with the presence of c-glide ²⁹; the two structures are isostructural with that of α-Ca₂SiO₄. ²³ For Na₂CrO₄(II), Ferrante ²⁶ reported the space group P6/mmc. The XRD analysis of Pistorius ²⁷ suggested that K₂CrO₄(II) has the same space group as K₂SO₄: P6/mmc, P6mc, P6̄2C, P3̄1C, or P31c.

Crystal structure information for phases of Na₂MoO₄ is summarized in Table 3.

Table 3 : Crystallographic data for phases of Na₂MoO₄

Phase	Crystal structure	T(°C)	Space group	Reference
Na ₂ MoO ₄ (I)	Cubic	< 458	-	30
			Fd3m	31
			-	32
			Fd3̄m	33

				34
				35
Na ₂ MoO ₄ (II)	Orthorhombic	458 to 592	-	32
			Pbn2 ₁	Ref. 10 in Ref. ³⁶
Na ₂ MoO ₄ (III)	Orthorhombic	592 to 641	-	32
			Fddd	Ref. 10 in Ref. ³⁶
				34
Na ₂ MoO ₄ (IV)	Hexagonal	641 to 687	P6 ₃ /mmc	Ref. 10 in Ref. ³⁶
				34
			-	32

The structure of the low-temperature phase (I) of Na₂MoO₄ is a spinel according to Lindqvist, ³⁰ with cubic crystal structure. ³⁰⁻³⁵ X-ray diffraction revealed the Fd $\bar{3}$ m space group, ³⁴ and further studies by Raman spectroscopy ³³ and neutron powder diffraction ³⁵ yielded the same space group. Swanson ³¹ reported the Fd3m space group. XRD patterns showed that the second phase (II) of Na₂MoO₄ is orthorhombic ^{32, 36} with space group Pbn2₁. ³⁶ The transition from II to III yielded the same crystal structure ^{32, 34, 36} with the Fddd space group. ^{34, 36} The high-temperature phase IV is hexagonal ^{32, 34, 36} with space group P6₃/mmc. ^{34, 36}

Crystal structure information for phases of K₂MoO₄ is summarized in Table 4.

Table 4 : Crystallographic data for phases of K₂MoO₄

Phase	Crystal structure	T(°C)	Space group	Reference
K ₂ MoO ₄ (I)	Monoclinic	< 324	C2/m	This work
				37
				38
			-	39
			C2/m	40
K ₂ MoO ₄ (II)	Orthorhombic	324 to 455	Ccmm	This work
			-	39
			Ccmm	41
K ₂ MoO ₄ (III)	Trigonal	455 to 928	P $\bar{3}$ m1	This work
			-	39
			P $\bar{3}$ m1	42

K_2MoO_4 exhibits three phases. The low-temperature form I is monoclinic. Our XRD analysis, the measurements of ³⁷ (who performed three-dimensional Patterson and Fourier syntheses that were refined by least squares techniques) and those of ³⁸⁻⁴⁰ confirmed $C2/m$ as the space group.

Our high-temperature XRD analysis showed that II is orthorhombic, in agreement with. ^{40, 41} The space group identified by us ($Ccmm$) agrees with that reported by Berg et al. ⁴¹

III has also been studied by us using high-temperature XRD up to 500 °C; analysis of the diffractogram indicated a trigonal structure. Akker et al. ⁴² erroneously reported an hexagonal structure. According to our results, the space group is $P\bar{3}m1$, in agreement with Akker et al. ⁴²

According to Warczewski, ³⁹ the transition from the intermediate-temperature phase II to the high-temperature pseudohexagonal phase III involves two modulated intermediate structures (incommensurable), which are orthorhombic and pseudohexagonal, respectively. Based on these data, K_2MoO_4 exhibits four phases, and the high-temperature form (IV) is hexagonal. However, as will be explained later, this fourth phase was not observed in our high-temperature XRD analysis (at 465 °C and 500 °C). Therefore, only three phases were considered for K_2MoO_4 in the present work.

Crystal structure information for phases of Na_2WO_4 is summarized in Table 5.

Table 5 : Crystallographic data for phases of Na_2WO_4

Phase	Crystal structure	$T(^{\circ}C)$	Space group	Reference
$Na_2WO_4(I)$	Cubic	< 588	Fd3m	43
			$Fd\bar{3}m$	44
				33
				35
				45
$Na_2WO_4(II)$	Tetragonal (tentative)	588 to 589	I41/amd (tentative)	45
$Na_2WO_4(III)$	Orthorhombic	589 to 694	$Pnam - D_{2h}^{16}$	43
			Fddd	45

There are some uncertainties in the literature regarding the number of phases for Na_2WO_4 , as well as their crystal structures and space groups. ^{33, 36, 43, 46-48} XRD analyses conducted by Pistorius ⁴³ and Temperature-Programmed X-ray powder Diffraction (TPXRD) by Hämmer and Höpfe ⁴⁵

suggested the presence of three phases. However, the XRD analyses performed by Pistorius ⁴³ have only identified with certainty two phases (I and III). For Na₂WO₄(II), the diffraction pattern was of rather poor quality.

XRD analysis, ⁴⁹ Raman spectroscopy ³³ and neutron diffraction ³⁵ confirmed that the low-temperature phase Na₂WO₄(I) is cubic with Fd $\bar{3}$ m space group. At room temperature, only Na₂MoO₄ and Na₂WO₄ exhibit an ordinary spinel structure among alkali metal sulfates, chromates, molybdates and tungstates. ^{30, 35} The work of Hämmer and Höpfe ⁴⁵ was the only one able to characterize the phase II using TPXRD; Austin and Pierce ⁴⁷ had indicated that both solid-solid transitions were displaced and non-reconstructive. Therefore, obtaining single crystals of the high-temperature phases of Na₂WO₄ by quenching was impossible, as well as the use of Rietveld refinement and differential scanning calorimetry. Based on TPXRD data, it is suggested that Na₂WO₄(II) has a tetragonal unit cell with lattice parameters $a = 1707.2$ pm, $c = 1293.6$ pm, and a space group consistent with symmetry relationships to Na₂WO₄(I), i.e. I41/amd. ⁴⁵ The latter is assumed to be a maximal subgroup of Fd $\bar{3}$ m and a direct supergroup of Fddd (space group of the phase III). ⁴⁵ Even with indexing and Pawley fitting ($R_{\text{Bragg}} = 0.013$, $R_{\text{wp}} = 0.058$), the structure of II was not reliably determined. Thus, Na₂WO₄(II) was assumed to crystallize in the I41/amd space group, with no symmetry relationship derivable between Na₂WO₄(I) and Na₂WO₄(III), and no proposed unit cell fitting into such a structure. ⁴⁵ Very limited high-temperature XRD studies have been conducted to identify the structure and space group of the phase III; Pistorius ⁴³ and Hämmer and Höpfe ⁴⁵ reported an orthorhombic structure with different space groups (Pnam and Fddd, respectively).

Crystal structure information for phases of K₂WO₄ is summarized in Table 6.

Table 6 : Crystallographic data for phases of K₂WO₄

Phase	Crystal structure	$T(^{\circ}\text{C})$	Space group	Reference
K ₂ WO ₄ (I)	Monoclinic	< 364	-	50
			C2/m	42
			-	39
K ₂ WO ₄ (II)	Orthorhombic (β -K ₂ SO ₄ type)	364 to 458	-	42
K ₂ WO ₄ (III)	Trigonal	458 to 927	P $\bar{3}$ m1	42
			-	39

K_2WO_4 displays three phases. The crystal structure was studied at room temperature by Raman spectroscopy⁵⁰ and XRD,^{39, 42} and was found to be monoclinic with C2/m space group.⁴² The phase II was examined by XRD only by Van Den Akker et al.,⁴² who suggested a β - K_2SO_4 type structure. However, the structure has not been reliably identified, and these authors indicated that most potassium salt phases have an orthorhombic structure (β - K_2SO_4 type).

For the phase III, the XRD analyses of Warczewski³⁹ and Van Den Akker et al.⁴² revealed a trigonal structure with $P\bar{3}m1$ space group.⁴² Note that³⁹ and⁴² incorrectly reported a hexagonal structure.

4. Selected thermodynamic properties for Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 and K_2WO_4

4.1 Sodium chromate

4.1.1 Transition temperature (T_{trs}) and enthalpy change (ΔH_{trs}) of solid-solid transition (I \rightarrow II) for Na_2CrO_4

To measure the temperature and enthalpy change for the solid-solid transition of Na_2CrO_4 , DSC measurements were conducted in this work. In addition, data acquired by various experimental techniques were collected from the literature and are shown in Table 7.

Table 7 : Transition temperature and enthalpy change of solid-solid transition for Na_2CrO_4

T_{trs} (I \rightarrow II) (°C)	ΔH_{trs} (I \rightarrow II) (kJ mol ⁻¹)	Experimental Method	Reference
417.3	8.49 \ddagger	DSC (2 nd heating) at 10 °C/min	This work
417.6	8.27 \ddagger	DSC (3 rd heating) at 10 °C/min	This work
413 \ddagger	-	Cooling curves	51
421 \pm 4	-	DTA*	52
420	10.04	DTA	53
420.9 \pm 3	9.58 \pm 0.42	Ice calorimetry, drop method	54
419	8.87 \ddagger	DTA	23

427‡	9.47	Calorimetry, drop method	26
419.4	10.06 (cooling) 9.60 (heating)	DSC 10 °C/min	55
419.1 ± 2.7	9.6 ± 0.6	Weighted average	This work

* The purity of salt is 99.5 %

‡ Outlier

4.1.2 Temperature (T_{fus}) and enthalpy of fusion (ΔH_{fus}) for Na_2CrO_4

The thermodynamic properties of fusion (temperature and enthalpy change) were measured by.^{26, 51, 53, 54, 56-64} The heat of fusion was obtained by drop calorimetry^{26, 54} and DTA.⁵³ In this work, DSC measurements were conducted. As an example, the DSC thermogram (2nd and 3rd heating/cooling cycles only) for Na_2CrO_4 is shown in Figure 1. The DSC thermograms for all other compounds are presented in the Supporting Information. All data collected from the literature and obtained in the present work are presented in Table 8.

Table 8 : Transition temperature and enthalpy of fusion for Na_2CrO_4

$T_{\text{fus}} (\text{II} \rightarrow \text{L})$ (°C)	$\Delta H_{\text{fus}} (\text{II} \rightarrow \text{L})$ (kJ mol ⁻¹)	Experimental Method	Reference
783‡	18.48‡	DSC (2 nd heating) at 10 °C/min	This work
783.4‡	19.60‡	DSC (3 rd heating) at 10 °C/min	This work
792	-	Cooling curves	51
780‡	-	Pt/Pt-Rh thermocouple; visual	56
794.5	-	Cooling curves	57
792	-	Calibrated TC; recorder potentiometer	58
791.9	-	DTA	59
793	-	Pt/Pt-Rh thermocouple; visual	60
796	25.15	DTA	53
792.4 ± 1	-	DTA; high- T microscopy	61
794	-	Visual-polythermal method	62
796.9 ± 2	24.23 ± 0.42	Ice calorimetry, drop method	54
792	24.31	Calorimetry*, drop method	26
785.6‡	-	DTA	63

795.1	-	DTA	64
793.3 ± 3.2	24.3 ± 0.9	Weighted average	This work

* The standard error is 0.07 % for the determination, and the absolute uncertainty of the enthalpy is estimated to be ± 0.3 %.

‡ Outlier

DSC(mW/mg)

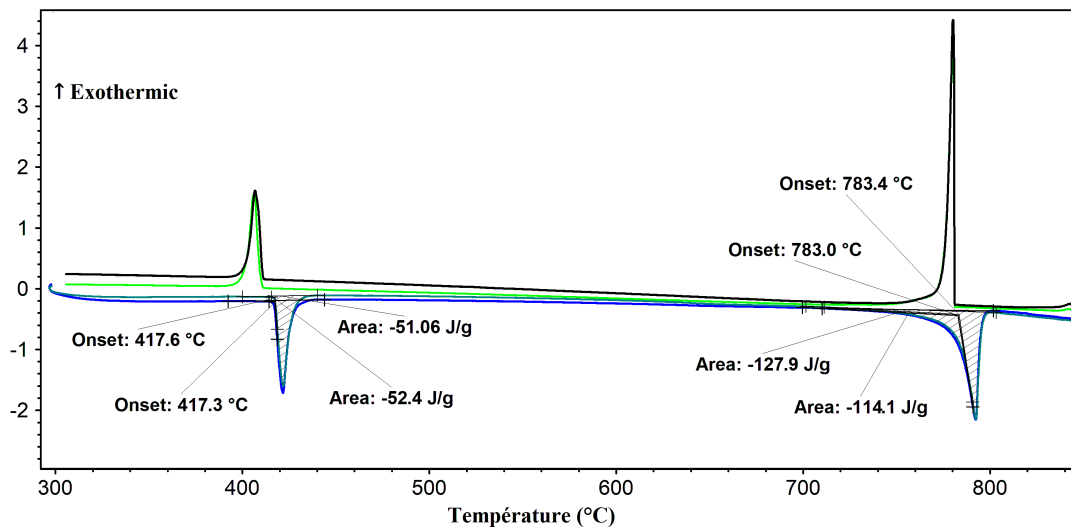


Figure 1 : Differential scanning calorimetry (DSC) thermogram for Na_2CrO_4 (2nd and 3rd heating/cooling cycles only). Blue: 2nd heating, dark green: 3rd heating, light green: 2nd cooling, black: 3rd cooling.

4.1.3 Recommended thermodynamic data for sodium chromate Na_2CrO_4

Our selected thermodynamic data ($\Delta_f H_{298}^\circ$, S_{298}° , and C_p) for sodium chromate (Na_2CrO_4) are provided in Table 9. For the pure liquid, below the temperature of fusion, the heat capacity (as a function of temperature) over a given temperature range was taken identical to that of the solid phase stable over this specific temperature range (i.e. C_p of the low-temperature phase I between 298.15 K and 692.3 K, and C_p of the high-temperature phase II between 692.3 K and 1066.4 K). Similarly, for solid II, below the temperature of the solid-solid transition, the heat capacity was taken identical to that of solid I. For all three phases, the heat capacity above the maximum temperature T_{\max} of the highest temperature range in Table 9 is assumed to be constant and equal to the value of C_p at T_{\max} .

The same approach was used for all other compounds considered in this work, even when there were more than two phases. More details on the thermodynamic properties selected for Na₂CrO₄ are given below.

Table 9 : Selected thermodynamic properties of Na₂CrO₄

Phase	T Range (K)	$\Delta_f H_{298}^\circ$ (kJ mol ⁻¹) ^a	S_{298}° (J mol ⁻¹ K ⁻¹) ^b	C_p (J mol ⁻¹ K ⁻¹)	Reference
Na ₂ CrO ₄ (I)	298.15	-1341.49			This work
			176.62		26
	298.15 to 692.3			101.07 + 0.13999 T/K	54
Na ₂ CrO ₄ (II)	298.15	-1331.86	190.52		This work
	298.15 to 692.3			101.07 + 0.13999 T/K	54
	692.3 to 1066.4			149.94 + 0.05159 T/K	54
Na ₂ CrO ₄ (L)	298.15	-1307.53	213.34		This work
	298.15 to 692.3			101.07 + 0.13999 T/K	54
	692.3 to 1066.4			149.94 + 0.05159 T/K	
	1066.4 to 2000			204.78	

^a Enthalpy relative to the enthalpy of the elements in their stable standard states at 298.15 K.

^b Absolute (third law) entropy.

The available measurements for the temperature and enthalpy change of the (I → II) and (II → L) transitions for Na₂CrO₄ are shown in Tables 7 and 8, respectively. For each property, the measured values were plotted as a function of the experiment number in order to identify visually outliers (see Figures S6, S7, S8 and S9 in the Supporting Information). A weighted average was then calculated from the retained measurements, with a weighting based on the expected accuracy of each experimental technique. The weighting factors used for the temperature and enthalpy change are given in Tables S3 and S4, respectively, in the Supporting Information. The standard deviation σ was then calculated.

The outliers are identified by the symbol ‡ in Tables 7 and 8 and are shown in red color in Tables S1 and S2 in the Supporting Information, and as empty circles in Figures S6, S7, S8 and S9 in the Supporting Information. In these scatter plots, the weighted average is shown as a solid line while the two dashed lines correspond to (weighted average $\pm 2\sigma$). It was checked that all outliers lie outside this range. The reported uncertainties in Tables 7 and 8 correspond to $\pm 2\sigma$. A similar approach was used for all other compounds investigated in this work.

The value of the standard enthalpy at 298.15 K ($\Delta_f H_{298}^\circ$) for $\text{Na}_2\text{CrO}_4(\text{I})$ was estimated as follows. The enthalpy of dissolution in water of $\text{Na}_2\text{CrO}_4(\text{I})$ ($\text{Na}_2\text{CrO}_{4(\text{I})} \rightarrow 2\text{Na}_{(\text{aq})}^+ + \text{CrO}_{4(\text{aq})}^{2-}$) was measured by calorimetry ⁶⁵ as $-19.12 \text{ kJ mol}^{-1}$. According to the most recent databases of the FactSage software package, ⁶⁶ $\Delta_f H_{298}^\circ(\text{Na}_{(\text{aq})}^+) = -239.73 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298}^\circ(\text{CrO}_{4(\text{aq})}^{2-}) = -881.15 \text{ kJ mol}^{-1}$. The obtained value of $-1341.49 \text{ kJ mol}^{-1}$ for $\Delta_f H_{298}^\circ(\text{Na}_2\text{CrO}_4(\text{I}))$ is very close to that of $-1342.20 \text{ kJ mol}^{-1}$ recommended in Barin's compilation. ⁶⁷ The Open Quantum Materials Database (OQMD) ^{68,69} reported an enthalpy of formation at 0 K of $-1331.21 \text{ kJ mol}^{-1}$ derived from Density Functional Theory (DFT) calculations. The corresponding value given in Materials Project ⁷⁰ is $-1343.37 \text{ kJ mol}^{-1}$.

The standard entropy at 298.15 K (S_{298}°) of $\text{Na}_2\text{CrO}_4(\text{I})$ was derived by Ferrante et al. ²⁶ as $176.62 \text{ J mol}^{-1} \text{ K}^{-1}$ by integration of their experimental C_p values from 5.5 K to 308.5 K using adiabatic calorimetry. This value is identical to that recommended in Barin's compilation ($176.61 \text{ J mol}^{-1} \text{ K}^{-1}$). ⁶⁷

To our knowledge, no other direct heat capacity measurements are available for Na_2CrO_4 . Denielou et al. ⁵⁴ carried out heat content measurements using drop calorimetry in an ice calorimeter. The salts were then analyzed using XRD to confirm that they were in their stable form. Enthalpy variations $H_T - H_{273}$ as a function of temperature were obtained as follows. For $\text{Na}_2\text{CrO}_{4(\text{I})}$, nine measurements were performed between 370 K and 665 K, and the following fit was provided by Denielou et al. ⁵⁴ : $H_T - H_{273} = 6.999 \times 10^{-5} T^2 + 10.107 \times 10^{-2} T - 32.78 \text{ kJ mol}^{-1}$ (0.4 %, empirical standard deviation of 0.03 kJ). ⁵⁴ For $\text{Na}_2\text{CrO}_{4(\text{II})}$, eleven measurements were conducted between 698 K and 1065 K, with the following fit : $H_T - H_{273} = 2.580 \times 10^{-5} T^2 + 14.994 \times 10^{-2} T - 35.84 \text{ kJ mol}^{-1}$ (0.15 %, empirical standard deviation of 0.03 kJ). ⁵⁴ Finally, for $\text{Na}_2\text{CrO}_{4(\text{L})}$, at least eleven measurements were made above 1091 K, with the following fit : $H_T - H_{273} = 20.478 \times 10^{-2} T - 40.74 \text{ kJ mol}^{-1}$ (0.11 %, empirical standard deviation of 0.05 kJ). ⁵⁴

For each phase of Na_2CrO_4 , the heat capacity expression (as a function of temperature) was derived by us from the fits of $H_T - H_{273}$ provided by Denielou et al. ⁵⁴ Calculated values of $H_T - H_{298}$ are compared to the available data in Figure 2. This figure includes the heat contents $H_T - H_{298}$ measured by Ferrante et al. ²⁶ as well as the $H_T - H_{298}$ values obtained by conversion of the $H_T - H_{273}$ data of Denielou et al. ⁵⁴ [$H_T - H_{298} = (H_T - H_{273}) - (H_{298} - H_{273})$]. These two series of data are in good agreement.

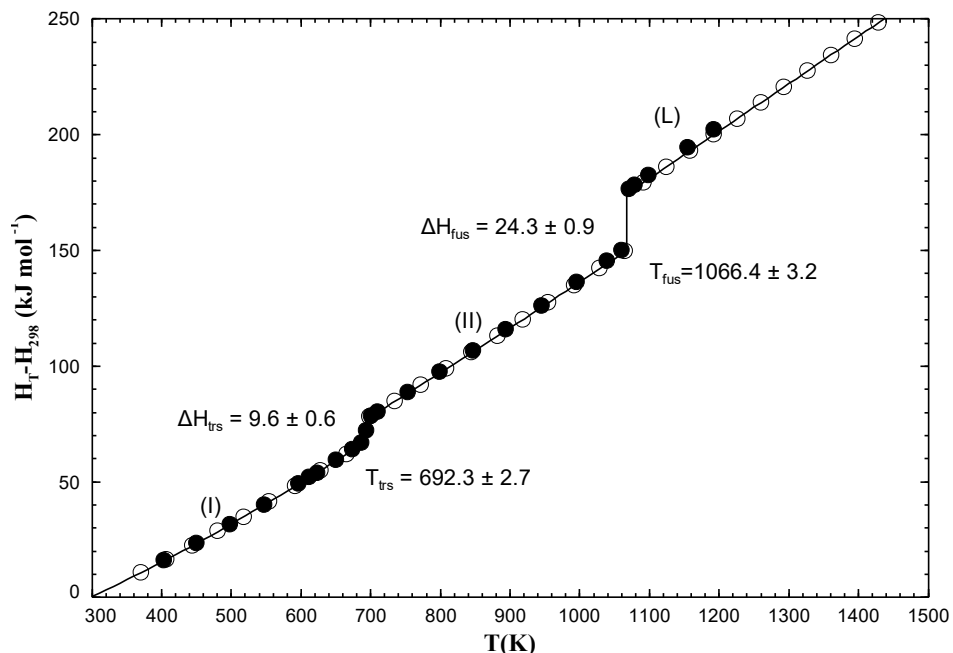


Figure 2 : Calculated heat content $H_T - H_{298}$ for Na_2CrO_4 (enthalpies of transition are the weighted average of all available data presented in tables 7 and 8). Experimental data from ²⁶ (●) and ⁵⁴ (○).

4.2 Potassium chromate

4.2.1 Transition temperature (T_{trs}) and enthalpy change (ΔH_{trs}) of solid-solid transition (I→II) for K_2CrO_4

The temperature and enthalpy change for the solid-solid transition of K_2CrO_4 was measured by DSC in the present work. These data along with all measurements collected from the literature (and obtained using various experimental techniques) are gathered in Table 10. Our experimental DSC thermogram is provided in the Supporting Information (Figure S1).

Table 10 : Transition temperature and enthalpy change of solid-solid transition for K_2CrO_4

T_{trs} (I → II) (°C)	ΔH_{trs} (I → II) (kJ mol ⁻¹)	Experimental Method	Reference
670.7	7.201	DSC (2 nd heating) at 10 °C/min	This work
671.2	7.123	DSC (3 rd heating) at 10 °C/min	This work

666	-	Heating or cooling curves	71
679‡	-	Pyrometry	72
669	-	Cooling curves	51
666	-	Cooling curves; visual	73
664	10.251‡	Heating or cooling curves	74
666.8	-	Thermocouple Pt-Rh	75
669	-	Cooling curves	76
663	-	Resistance technique	27
671	7.155	DTA	53
665	10.2‡	-	77
668.5 ± 3	-	DTA*	78
675	-	DTA**	79
662.9 ± 3	9.954 ± 0.502‡	Ice calorimeter, enthalpimetry	80
674	6.583	DSC*** at 5 °C/min	81
	5.243‡	DTA*** at 5 °C/min	
670.2 ± 3	7.2 ± 0.25	DSC 10 °C/min (heating) 40 °C/min (cooling)	82
	6.908****		
668.9	-	Elect Conduct (single crystal)	83
669.2 ± 7.1	7.0 ± 0.5	Weighted average	This work

* The purity of this salt is 99.8 %

** The purity of this salt is 99.96 %

*** The purity of this salt is 99.87 %

**** Questionable according to the authors

‡ Outlier

4.2.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for K_2CrO_4

The temperature and enthalpy of fusion have been measured by.^{51, 53, 59, 61, 71-73, 75, 77, 80, 84-88} The heat of fusion was obtained by enthalpimetric analysis⁸⁰ and DTA.⁵³ All data from the literature and our DSC measurements are given in Table 11.

Table 11 : Transition temperature and enthalpy of fusion for K_2CrO_4

$T_{fus}(II \rightarrow L)$ (°C)	$\Delta H_{fus}(II \rightarrow L)$ (kJ mol ⁻¹)	Experimental Method	Reference
977.2	32.896	DSC (2 nd heating) at 10 °C/min	This work
976.4	34.197	DSC (3 rd heating) at 10 °C/min	This work
971	-	Heating or cooling curves	71
984	-	Pyrometry	72
976	-	Cooling curves	51
978	-	Cooling curves; visual	73
968.3	-	Thermocouple Pt-Rh	75
970.9	-	Cooling curves	84
976	-	DTA	59
972	-	Visual-polythermal method	85
979	31.547	DTA	53
984	28.9‡	-	77
980	-	DTA and high-temperature microscopy	61
984	-	DTA	86
976	-	Visual-polythermal method	87
968	-	Pt/Pt-Rh thermocouple; visual	88
973.9 ± 4	32.991 ± 0.669	Ice calorimeter, enthalpimetry	80
975.9 ± 9.9	33.1 ± 1.8	Weighted average	This work

‡ Outlier

4.2.3 Recommended thermodynamic data for potassium chromate K_2CrO_4

Our selected thermodynamic data ($\Delta_f H_{298}^\circ$, S_{298}° , and C_p) for potassium chromate (K_2CrO_4) are given in Table 12.

Table 12 : Selected thermodynamic properties of K_2CrO_4

Phase	T Range (K)	$\Delta_f H_{298}^\circ$ (kJ mol ⁻¹)	S_{298}° (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	Reference
K_2CrO_4 (I)	298.15	-1403.70			89
			199.99		90
	298.15 to 942.4			$144.28 + 0.06119 T/K$	80
K_2CrO_4 (II)	298.15	-1396.66	207.47		This work
	298.15 to 942.4			$144.28 + 0.06119 T/K$	80
	942.4 to 1249.1			$44.89 + 0.15339 T/K$	
	1249.1 to 2000*			212.01	
K_2CrO_4 (L)	298.15	-1363.55	233.97		This work
	298.15 to 942.4			$144.28 + 0.06119 T/K$	80
	942.4 to 1249.1			$44.89 + 0.15339 T/K$	
	1249.1 to 2000			212.01	

* : Above the temperature of fusion, the heat capacity of K_2CrO_4 (II) was assumed to be equal to that of K_2CrO_4 (L) to ensure a reasonable extrapolation of the Gibbs energy at high temperatures. In absence of this additional C_p range, the high-temperature phase would be calculated to be more stable than the pure liquid above 6814 K.

The standard enthalpy at 298.15 K of $-1403.70 \text{ kJ mol}^{-1}$ for K_2CrO_4 (I) was taken directly from the NBS Tables of chemical thermodynamic properties of Wagman et al.,⁸⁹ since no experimental values were found in the literature. OQMD^{68, 69} reported an enthalpy of formation at 0 K of $-1362.95 \text{ kJ mol}^{-1}$ using DFT calculations. The corresponding value given in Materials Project⁷⁰ is $-1394.70 \text{ kJ mol}^{-1}$.

The standard entropy at 298.15 K (S_{298}°) reported by Popov and Kolesov⁹⁰ (see Table 12) is in very good agreement with that in the book edited by Lax⁷⁷ (i.e. $200 \text{ J mol}^{-1} \text{ K}^{-1}$), and also with that from Barin⁶⁷ (i.e. $199.99 \text{ J mol}^{-1} \text{ K}^{-1}$). The value from Popov and Kolesov is the only experimental value found in the literature; it was obtained by integration of $\int_0^{298.15 \text{ K}} \frac{C_p}{T} dT$, where the low-temperature heat capacity was measured by calorimetry.

To our knowledge, there are no other direct C_p measurements for K_2CrO_4 available in the literature. Heat content ($H_T - H_{298}$) measurements were conducted by Sirousse-Zia⁸⁰ using 99.5 % certified material and enthalpimetric analysis in an ice calorimeter. This author obtained eleven experimental values for each phase ($K_2CrO_{4(I)}$, $K_2CrO_{4(II)}$, and $K_2CrO_{4(L)}$), and derived a fit of $H_T - H_{298}$ as a function of temperature. For I, between 517 and 888 K, $H_T - H_{298} = 3.622 \times 10^{-8} T^3 - 2.227 \times 10^{-5} T^2 + 16.336 \times 10^{-2} T - 45.89 \text{ kJ mol}^{-1}$ (0.7 %, empirical standard deviation of 0.06 kJ). The corresponding value is 1.776 kJ mol⁻¹ at 298.15 K. The following new fit, which is null at 298.15 K, was obtained by us : $3.059523 \times 10^{-5} (T - 298.15)^2 + 1.625099 \times 10^{-1} (T - 298.15) \text{ kJ mol}^{-1}$.

Sirousse-Zia⁸⁰ also derived the following fits : for II, between 942 K and 1202 K, $H_T - H_{298} = 7.669 \times 10^{-5} T^2 + 4.489 \times 10^{-2} T + 17.95 \text{ kJ mol}^{-1}$ (0.4 %, empirical standard deviation of 0.05 kJ); for the pure liquid, above 1261 K, $H_T - H_{298} = 2.120 \times 10^{-1} T - 38.17 \text{ kJ mol}^{-1}$ (0.4 %, empirical standard deviation of 0.05 kJ). For each phase of K_2CrO_4 , the heat capacity expression (as a function of temperature) was derived (see Table 12) from the fits of $H_T - H_{298}$ given previously. Calculated values of $H_T - H_{298}$ are shown along with the available data in Figure 3. Our calculations somewhat underestimate the measurements of Sirousse-Zia⁸⁰ for the high-temperature phase and the pure liquid since the selected enthalpy changes for the solid-solid transition and the fusion are weighted averages of all available data from the literature and of our own DSC measurements.

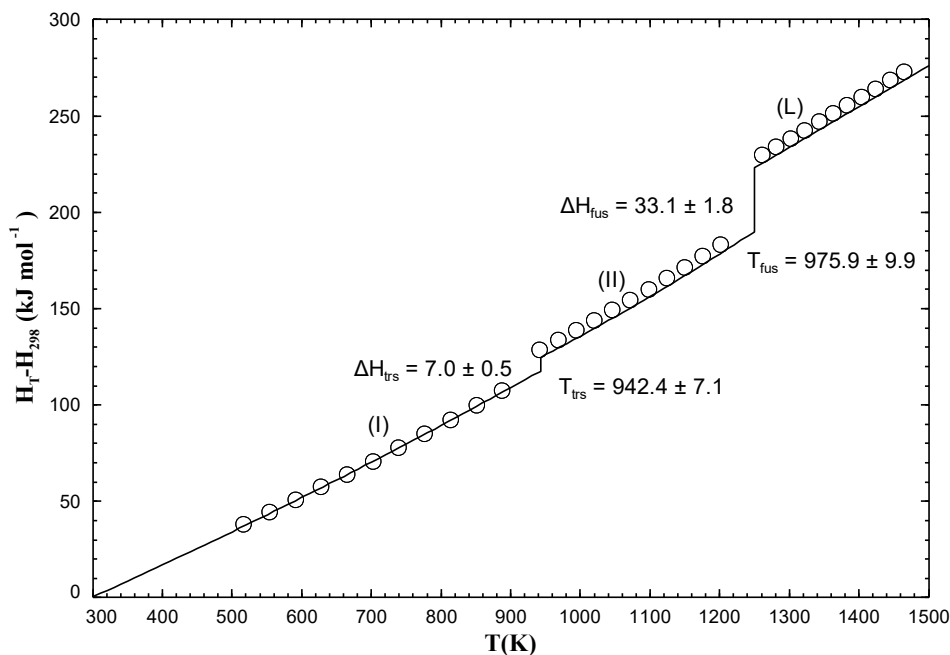


Figure 3 : Calculated heat content $H_T - H_{298}$ for K_2CrO_4 (enthalpies of transition are the weighted average of all available data presented in tables 10 and 11). Experimental data from ⁸⁰ (○).

4.3 Sodium molybdate

4.3.1 Transition temperature (T_{trs}) and enthalpy change (ΔH_{trs}) of solid-solid transitions (I→II, II→III, and III→IV) for Na_2MoO_4

The temperatures and enthalpy changes for the various solid-solid transitions (I→II, II→III, and III→IV) of Na_2MoO_4 were measured by DSC in this work. These data along with all measurements available in the literature are shown in Tables 13, 14 and 15, respectively. Our experimental DSC thermogram is presented in the Supporting Information (Figure S2).

Table 13 : Transition temperature and enthalpy change of transition I→II for Na_2MoO_4

T_{trs} (I→II) (°C)	ΔH_{trs} (I → II) (kJ mol ⁻¹)	Experimental Method	Reference
455.8	22.447	DSC (2 nd heating) at 10 °C/min	This work
456.7	22.097	DSC (3 rd heating) at 10 °C/min	This work
440‡	61.086‡	Heating or cooling curves	74
457.9 ± 2	26.65	DTA	53
454.9 ± 1	-	DTA at 5 °C/min	91
444.9 ± 2‡	21.76 ± 0.38	Calorimetry, drop method	54
460.9	-	DSC (cooling) at 3 °C/min	36
‡ 440.9 (run 1) 435.9 (run 2) 441.9 (run 3)	-	DTA (1.8 °C/min & 10.2 °C/min)	92
459.9	-	DTA (heating) at 10 °C/min	32
457.85	-	DSC at 10 °C/min	
509.9-529.9‡	-	Raman spectroscopy	33
456.9 ± 1	26.78 ± 0.38	DSC (10, 5 & 2 °C/min)	93
457.6 ± 3.7	23.1 ± 4.9	Weighted average	This work

‡ Outlier

Table 14 : Transition temperature and enthalpy change of transition II→III for Na₂MoO₄

$T_{\text{trs}}(\text{II} \rightarrow \text{III})$ (°C)	$\Delta H_{\text{trs}}(\text{II} \rightarrow \text{III})$ (kJ mol ⁻¹)	Experimental Method	Reference
591.4	1.685	DSC (2 nd heating) at 10 °C/min	This work
591.4	1.700	DSC (3 rd heating) at 10 °C/min	This work
590.9 ± 2	1.88	DTA	53
579.9 ± 2‡	-	DTA at 5 °C/min	91
592.9 ± 3	2.09 ± 0.38	Calorimetry, drop method	54
591.9	-	DSC (cooling) at 3 °C/min	36
‡ 571.9 (run 1) 574.9 (run 2) 569.9 (run 3)	-	DTA (1.8 & 10.2 °C/min)	92
579.9‡	-	DTA (heating) at 10 °C/min	32
591.9	-	DSC at 10 °C/min	
549.9-639.9	-	Raman spectroscopy	33
592.9 ± 1	2.01 ± 0.33	DSC (10, 5 & 2 °C/min)	93
591.8 ± 2.5	1.9 ± 0.3	Weighted average	This work

‡ Outlier

Table 15 : Transition temperature and enthalpy change of transition III→IV for Na₂MoO₄

$T_{\text{trs}}(\text{III} \rightarrow \text{IV})$ (°C)	$\Delta H_{\text{trs}}(\text{III} \rightarrow \text{IV})$ (kJ mol ⁻¹)	Experimental Method	Reference
642.4	8.316	DSC (2 nd heating) at 10 °C/min	This work
642.4	8.248	DSC (3 rd heating) at 10 °C/min	This work
641.9 ± 2	10.84‡	DTA	53
637.9 ± 2	-	DTA at 5 °C/min	91
641.9 ± 2	8.28 ± 0.46	Calorimetry, drop method	54
639.9	-	DSC (cooling) at 3 °C/min	36

641.9 ± 2	8.3 ± 0.4	Calorimetry ; spectroscopy	94
‡ 622.9 (run 1) 625.9 (run 2) 618.9 (run 3)	-	DTA (1.8 & 10.2 °C/min)	92
641.85	-	DTA (heating) at 10 °C/min	32
637.9	-	DSC at 10 °C/min	
669.9-676.9‡	-	Raman spectroscopy	33
639.9 ± 1	7.81 ± 1.25	DSC (10, 5 & 2 °C/min)	93
640.6 ± 3.4	8.2 ± 0.4	Weighted average	This work

‡ Outlier

4.3.2 Temperature (T_{fus}) and enthalpy of fusion (ΔH_{fus}) for Na_2MoO_4

The properties of fusion (temperature and enthalpy change) were measured by.^{32, 36, 53, 54, 91-97} The enthalpy of fusion was obtained using DTA,⁵³ drop calorimetry,⁵⁴ calorimetry,⁹⁴ and DSC.⁹³ All data collected from the literature and our own DSC measurements are displayed in Table 16.

Table 16 : Transition temperature and enthalpy of fusion for Na_2MoO_4

$T_{\text{fus}}(\text{IV} \rightarrow \text{L})$ (°C)	$\Delta H_{\text{fus}}(\text{IV} \rightarrow \text{L})$ (kJ mol ⁻¹)	Experimental Method	Reference
688.2	18.637	DSC (2 nd heating) at 10 °C/min	This work
686.9	18.495	DSC (3 rd heating) at 10 °C/min	This work
688	-	Visual-polythermal method	95
690	-	DTA	96
692.9 ± 2‡	24.43‡	DTA	53
686.9 ± 1	-	DTA at 5 °C/min	91
688.9 ± 3	21.42 ± 0.5	Calorimetry, drop method	54
688.9	-	DSC (cooling) at 3 °C/min	36
685.9 ± 2	20.4 ± 0.4	Calorimetry; spectroscopy	94

687	-	Thermal analysis	97
‡ 671.9 (run 1) 674.9 (run 2) 667.9 (run 3)	-	DTA (1.8 & 10.2 °C/min)	92
679.9‡	-	DSC at 10 °C/min	32
684.9	-	DTA at 10 °C/min	
683.9 ± 1	20.73 ± 1.14	DSC (10, 5 & 2 °C/min)	93
687.1 ± 3.5	20.4 ± 2.5	Weighted average	This work

‡ Outlier

4.3.3 Recommended thermodynamic data for sodium molybdate Na_2MoO_4

Our selected thermodynamic data ($\Delta_f H_{298}^\circ$, S_{298}° , and C_p) for sodium molybdate (Na_2MoO_4) are shown in Table 17.

Table 17 : Selected thermodynamic properties of Na_2MoO_4

Phase	T Range (K)	$\Delta_f H_{298}^\circ$ (kJ mol ⁻¹)	S_{298}° (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	Reference
$\text{Na}_2\text{MoO}_4(\text{I})$	298.15	-1465.87			98
			159.41		99
	298.15 to 730.7			125.34 + 0.07858 T/K	54
$\text{Na}_2\text{MoO}_4(\text{II})$	298.15	-1442.80	190.98		This work
	298.15 to 730.7			125.34 + 0.07858 T/K	54
	730.7 to 865			-215.46 + 0.50643 T/K	
$\text{Na}_2\text{MoO}_4(\text{III})$	298.15	-1440.86	193.22		This work
	298.15 to 730.7			125.34 + 0.07858 T/K	54
	730.7 to 865			-215.46 + 0.50643 T/K	
	865 to 913.7			202.30	This work
$\text{Na}_2\text{MoO}_4(\text{IV})$	298.15	-1432.63	202.23		This work
	298.15 to 730.7			125.34 + 0.07858 T/K	54
	730.7 to 865			-215.46 + 0.50643 T/K	
	865 to 913.7			202.30	This work
	913.7 to 960.2			208.30	
$\text{Na}_2\text{MoO}_4(\text{L})$	298.15	-1412.26	223.45		This work

	298.15 to 730.7			$125.34 + 0.07858 T/K$	54
	730.7 to 865			$-215.46 + 0.50643 T/K$	
	865 to 913.7			202.30	This work
	913.7 to 960.2			208.30	
	960.2 to 2000			213.00	54

The molar enthalpy of dissolution of Na_2MoO_4 in a NaOH solution was measured at 298.15 K by Tangri et al. using an isoperibol calorimeter.⁹⁸ The molar enthalpy of solution at infinite dilution was measured as $-11.79 \pm 0.51 \text{ kJ mol}^{-1}$,⁹⁸ and a standard enthalpy at 298.15 K of $-1465.87 \text{ kJ mol}^{-1}$ was then derived for $\text{Na}_2\text{MoO}_4(\text{I})$. Using a cycle of calorimetric reactions, Koehler et al.¹⁰⁰ evaluated $\Delta_f H_{298}^\circ = -1467.75 \text{ kJ mol}^{-1}$. The value recommended in Barin's compilation tables⁶⁷ is $-1469.00 \text{ kJ mol}^{-1}$. The $\Delta_f H_{298}^\circ$ value reported by Tangri et al.⁹⁸ was selected in the present work. OQMD^{68, 69} reported an enthalpy of formation at 0 K of $-1560.17 \text{ kJ mol}^{-1}$ using DFT. The corresponding value given in Materials Project⁷⁰ is $-1456.16 \text{ kJ mol}^{-1}$.

For the standard entropy at 298.15 K (S_{298}°), Welle and King⁹⁹ reported a value of $159.41 \text{ J mol}^{-1} \text{ K}^{-1}$, estimated by integration of their low-temperature heat capacity measurements obtained by calorimetry. The Einstein and Debye functions were used over the extrapolated temperature range of 0 K to 51 K.

Using adiabatic calorimetry, Gavrichev et al.¹⁰¹ performed low-temperature C_p measurements from 14 K to 297 K, and derived a S_{298}° value of $149.9 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$.

Finally, the S_{298}° value obtained by Weller and King,⁹⁹ which is close to the value of $159.41 \text{ J mol}^{-1} \text{ K}^{-1}$ recommended in Barin's compilation tables,⁶⁷ was selected in this work.

Using drop calorimetry in an ice calorimeter, Denielou et al.⁵⁴ performed heat content measurements ($H_T - H_{273}$) for Na_2MoO_4 , and derived fits of their data along with C_p expressions (as a function of temperature). The stability of the salts was verified by XRD analyses.

For $\text{Na}_2\text{MoO}_4(\text{I})$, based on eleven measurements between 427 K and 709 K, $H_T - H_{273} = 3.929 \times 10^{-5} T^2 + 1.253 \times 10^{-1} T - 376.02 \text{ kJ mol}^{-1}$ (0.3 %, empirical standard deviation of 0.02 kJ). This fit was assumed to be valid from 298.15 K to our selected temperature of 730.7 K for the I→II transition.

Extrapolation to 296.5 K of the heat capacity expression $C_{p(\text{I})} = 0.07858 T + 125.34427 \text{ J mol}^{-1} \text{ K}^{-1}$ (valid from 427 K to 709 K) given by Denielou et al.⁵⁴ gives a value of $148.64 \text{ J mol}^{-1} \text{ K}^{-1}$, which

agrees well with the heat capacity measurement of Weller and King.⁹⁹ Gavrichev et al.¹⁰¹ measured at 298.15 K a value of 131.81 J mol⁻¹ K⁻¹, which is about 17 J mol⁻¹ K⁻¹ lower.

For Na₂MoO₄(II), based on twelve measurements between 734 K and 857 K, $H_T - H_{273} = 2.532 \times 10^{-4}T^2 - 2.155 \times 10^{-1}T + 118.59$ kJ mol⁻¹ (0.13 %, empirical standard deviation of 0.05 kJ). This fit was assumed to be valid from 730.7 K to our selected temperature of 865 K for the II→III transition.

For Na₂MoO₄(III), based on ten measurements between 870 K and 907 K, $H_T - H_{273} = 4.456 \times 10^{-4}T^2 - 5.895 \times 10^{-1}T + 300.54$ kJ mol⁻¹ (0.14 %, empirical standard deviation of 0.04 kJ). This fit was assumed to be valid from 865 K to our selected temperature of 913.7 K for the III→IV transition.

A typo was detected in the article of Denielou et al.⁵⁴ The original constant of 30.054 kJ mol⁻¹ in the fit provided for Na₂MoO₄(III) corresponded to negative values of $(H_T - H_{273})$. Adjusting this constant to 300.54 kJ mol⁻¹ permitted us to reproduce (within the reported error bars) the experimental enthalpy changes of Denielou et al.⁵⁴ for the II→III and III→IV transitions (the two temperatures used for these calculations were those reported by the authors).

For Na₂MoO₄(IV), based on nine measurements between 920 K and 960 K, $H_T - H_{273} = -4.774 \times 10^{-4}T^2 + 1.106T + 469.86$ kJ mol⁻¹ (0.16 %, empirical standard deviation of 0.08 kJ). This fit was assumed to be valid from 913.7 K to our selected temperature of fusion of 960.2 K.

A marked decrease of C_p as a function of temperature was observed between the phases III and IV, owing to the mathematical expressions of $(H_T - H_{273})$ proposed by Denielou et al.⁵⁴ Since the temperature ranges of validity were very limited (from 870 K to 907 K for III, and from 920 K to 960 K for IV), the corresponding values of $(H_T - H_{273})$ were refitted by us using a linear expression $(a + bT)$, thus leading to constant heat capacity values. Our new fits of $(H_T - H_{273})$ are $2.023 \times 10^{-1}T - 51.169$ (kJ mol⁻¹) for III, and $2.083 \times 10^{-1}T - 48.12$ (kJ mol⁻¹) for IV. The corresponding C_p values are 202.3 J mol⁻¹ K⁻¹ and 208.3 J mol⁻¹ K⁻¹, respectively (see Table 17).

For Na₂MoO₄(L), based on fourteen measurements above 1091 K, $H_T - H_{273} = 2.0478 \times 10^{-1}T - 40.74$ kJ mol⁻¹ (0.1 %, empirical standard deviation of 0.12 kJ).

Calculated values of $H_T - H_{298}$ are shown along with the available measurements in Figure 4. This figure includes the heat contents $H_T - H_{298}$ measured by Iyer et al.⁹² as well as the $H_T - H_{298}$ values obtained by conversion of the $H_T - H_{273}$ data of Denielou et al.⁵⁴ [$H_T - H_{298} = (H_T - H_{273}) - (H_{298} - H_{273})$]. These two series of data are in good agreement.

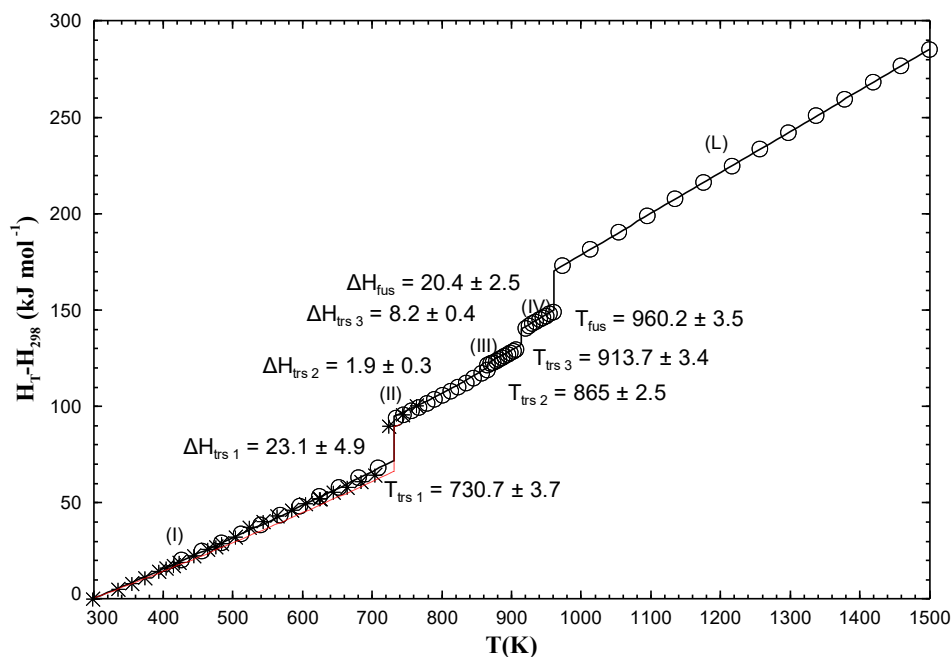


Figure 4 : Calculated heat content $H_T - H_{298}$ for Na_2MoO_4 (enthalpies of transition are the weighted average of all available data presented in tables 13 to 16). Experimental data from ⁵⁴ (○) and ⁹² (*). Red dashed line : $H_T - H_{298}$ fit of low-temperature heat capacity data shown in Figure 5.

The calculated heat capacity at low temperatures for $\text{Na}_2\text{MoO}_4(\text{I})$ is shown in Figure 5 along with the measurements of Weller and King,⁹⁹ Gavrichev et al.,¹⁰¹ and Zhidikova and Kuskov.¹⁰²

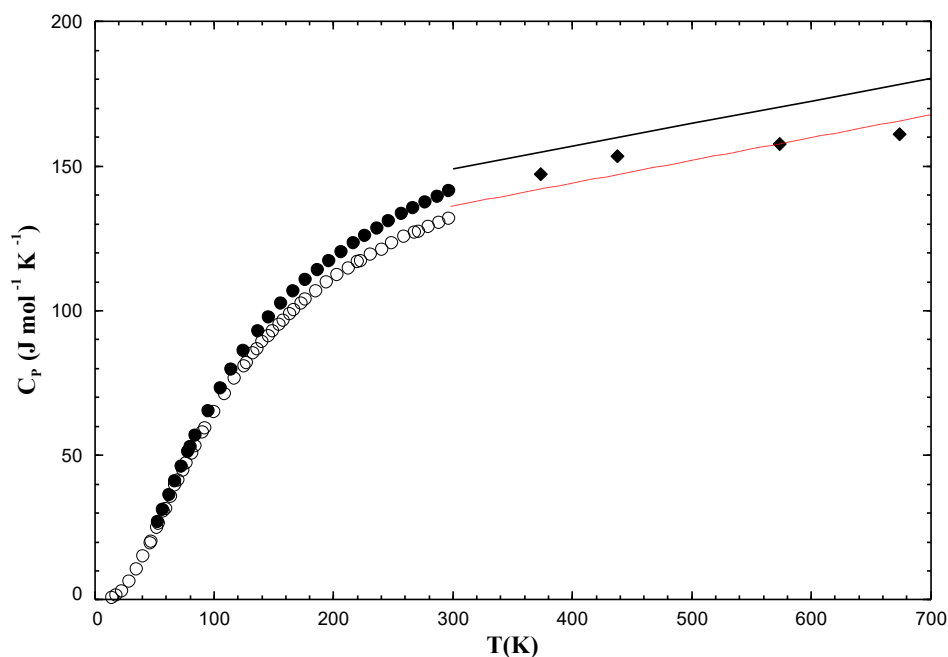


Figure 5 : Calculated heat capacity at low temperatures for Na₂MoO₄(I). Experimental data from ⁹⁹ (●), ¹⁰¹ (○), and ¹⁰² (◆). Red dashed line : best linear fit of C_P data above room temperature.

In Figure 4, the black full lines correspond to our final calculations while the red dashed line corresponds to heat contents $H_T - H_{298}$ obtained from the fit of the low-temperature C_P data measured by ⁹⁹, ¹⁰¹, and ¹⁰², and shown in Figure 5. An average deviation of about 3.7 kJ mol⁻¹ is observed for the red dashed line, which is substantially higher than the error of about 0.02 kJ mol⁻¹ reported by. ⁵⁴ This lends support to our final calculations displayed in Figures 4 and 5.

The heat content measurements of Iyer et al. ⁹² were carried out over the temperature range 335 K to 760 K using drop calorimetry in a high-temperature Calvet calorimeter. These authors observed transitions at 520 ± 5 K and 720 ± 5 K. The first transition (at about 520 K) has not been reported previously while the DTA study of the same authors from 300 K to 973 K revealed the presence of three solid-solid transitions (at about 713 K, 845 K and 896 K). According to Iyer et al., ⁹² the first transition (at about 520 K) was not observed in their calorimetric study owing to the sensitivity being insufficient to detect a small enthalpy change for a small sample size. For the second transition (at about 720 K), there is good agreement between the calorimetric and DTA studies of Iyer et al., ⁹² and also with the calorimetric measurements of Denielou et al. ⁵⁴ using drop calorimetry in an ice calorimeter. Finally, the transition at about 520 K reported by Iyer et al. ⁹² was ignored in the present work, and only three solid-solid transitions (corresponding to the four phases I, II, III, and IV) were considered.

4.4 Potassium molybdate

4.4.1 Transition temperature (T_{trs}) and enthalpy change (ΔH_{trs}) of solid-solid transitions (I→II, II→III, and III→IV) for K₂MoO₄

The temperatures and enthalpy changes for the various solid-solid transitions (I→II, II→III, and III→IV) of K₂MoO₄ were measured by DSC in the present work. These measurements along with all data collected from the literature are displayed in Tables 18, 19 and 20, respectively. Our experimental DSC thermogram is provided in the Supporting Information (Figure S3).

Table 18 : Transition temperature and enthalpy change of transition I→II for K₂MoO₄

$T_{\text{trs}}(\text{I} \rightarrow \text{II})$ (°C)	$\Delta H_{\text{trs}}(\text{I} \rightarrow \text{II})$ (kJ mol ⁻¹)	Experimental Method	Reference
325.4	2.338‡	DSC (2 nd heating) at 10 °C/min	This work
322.2	2.236‡	DSC (3 rd heating) at 10 °C/min	This work
327 ± 1.5	-	Thermal study	103
323	-	Thermal analysis (cooling)	104
321	-	Thermal analysis	59
323	-	DTA	91
295.9 ± 2‡	11.34	DTA	53
282.9‡	8.27 ± 0.10	DTA Heating 0.5 °C/min Cooling 0.42 °C/min	105
322.9 ± 1	11.34 ± 1.62	DSC (5 & 10 °C/min)	40
323.5 ± 3.8	10.6 ± 2.9	Weighted average	This work

‡ Outlier

Table 19 : Transition temperature and enthalpy change of transition II→III for K₂MoO₄

$T_{\text{trs}}(\text{II} \rightarrow \text{III})$ (°C)	$\Delta H_{\text{trs}}(\text{II} \rightarrow \text{III})$ (kJ mol ⁻¹)	Experimental Method	Reference
454.8	0.980	DSC (2 nd heating) at 10 °C/min	This work
455.1	0.978	DSC (3 rd heating) at 10 °C/min	This work
454 ± 1.5	-	Thermal study	103
458	-	Thermal analysis (cooling)	104
439‡	-	Thermal analysis	59
438‡	-	DTA	91
451.9 ± 2	1.13	DTA	53
456.9	0.64 ± 0.03‡	DTA	105

		Heating 0.5 °C/min Cooling 0.42 °C/min	
452.9 ± 2	1.04 ± 0.06	DSC (5 & 10 °C/min)	⁴⁰
454.7 ± 3.9	1.0 ± 0.1	Weighted average	This work

‡ Outlier

Table 20 : Transition temperature and enthalpy change of transition III→IV for K₂MoO₄

$T_{\text{trs}}(\text{III} \rightarrow \text{IV})$ (°C)	$\Delta H_{\text{trs}}(\text{III} \rightarrow \text{IV})$ (kJ mol ⁻¹)	Experimental Method	Reference
-	-	DSC (2 nd heating) at 10 °C/min	This work
-	-	DSC (3 rd heating) at 10 °C/min	This work
479.0 ± 1.5	-	Thermal study	¹⁰³
480	-	Thermal analysis (cooling)	¹⁰⁴
475	-	Thermal analysis	⁵⁹
462	-	DTA	^{91*}
475.9 ± 10	-	-	Reported from “V. P. Glushko (VINITI, Moscow, 1981–1982) volume 10” in ⁴⁰
479.9	0.024	DSC 5 °C/min	⁴⁰

* Another solid-solid transition at 480 °C, which was not considered in this work, has been reported by. ⁹¹

The experimental data in Tables 18, 19, and 20 suggest that there are three different solid-solid transitions for K₂MoO₄. According to our high-temperature XRD measurements (at 465 °C and 500 °C), there are only two solid-solid transitions. Furthermore, in the second and third heating/cooling runs of our two DSC experiments, the III→IV transition was never observed. While performing DSC measurements with a heating/cooling rate of 5 K/min, Gavrichev et al. ⁴⁰ did observe the III→IV transition and reported an extremely low enthalpy change of 0.024 kJ mol⁻¹. ⁴⁰ Other studies reported a similar transition temperature ^{59, 91, 103, 104} but did not measure the corresponding enthalpy change.

In most studies reporting the III→IV transition, the purity of the reagents was not indicated, and thus this transition may be due to the presence of impurities. Finally, based on our XRD and DSC measurements, only two solid-solid transitions were considered for K₂MoO₄ in the present work. Note that, if a III→IV transition were taken into account, it would have very little impact on our future calculations related to high temperature corrosion, since the corresponding enthalpy change would be very small (0.024 kJ mol⁻¹) and the phase III would be stable over a limited temperature range of less than 25 °C (i.e. between about 455 °C and 478 °C).

4.4.2 Temperature (T_{fus}) and enthalpy of fusion (ΔH_{fus}) for K₂MoO₄

The properties of fusion (temperature and enthalpy change) were measured by.^{40, 53, 59, 94-97, 103-105}

The heat of fusion was measured by DTA,^{53, 105} calorimetry,⁹⁴ and DSC,⁴⁰. All experimental data from the literature and our own DSC measurements are gathered in Table 21.

Table 21 : Transition temperature and enthalpy of fusion for K₂MoO₄

T_{fus} (III→L) (°C)	ΔH_{fus} (III→L) (kJ mol ⁻¹)	Experimental Method	Reference
927.1	30.460‡	DSC (2 nd heating) at 10 °C/min	This work
927.8	28.983‡	DSC (3 rd heating) at 10 °C/min	This work
819 ± 1.5‡	-	Thermal study	103
926	-	Thermal analysis (cooling)	104
936	-	Thermal analysis	59
926	-	Visual-polythermal method	95
926	-	Heating curves	96
926	38.702	DTA	53
925.9 ± 1	38.70	DTA Heating at 0.5 °C/min Cooling at 0.42 °C/min	105
927.9 ± 2	34.70 ± 0.7	Calorimetry; spectroscopy	94
926	-	Thermal analysis	97
930.9 ± 1	40.14 ± 1.25	DSC (5 & 10 °C/min)	40
927.8 ± 5.9	36.6 ± 5.0	Weighted average	This work

‡ Outlier

4.4.3 Recommended thermodynamic data for potassium molybdate K_2MoO_4

Our selected thermodynamic data ($\Delta_f H_{298}^\circ$, S_{298}° and C_p) for potassium molybdate (K_2MoO_4) are shown in Table 22.

Table 22 : Selected thermodynamic properties of K_2MoO_4

Phase	T Range (K)	$\Delta_f H_{298}^\circ$ (kJ mol ⁻¹)	S_{298}° (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	Reference
$K_2MoO_4(I)$	298.15	-1497.85			This work
			199.30		40
	298.15 to 596.6			$113.50 + 0.09688 T/K + 729689.6 (T/K)^{-2}$	This work
$K_2MoO_4(II)$	298.15 to 727.9	-1487.27	217.02	$113.50 + 0.09688 T/K + 729689.6 (T/K)^{-2}$	This work
$K_2MoO_4(III)$	298.15 to 730.7	-1486.26	218.42	$113.50 + 0.09688 T/K + 729689.6 (T/K)^{-2}$	This work
	730.7 to 865			$-227.31 + 0.52473 T/K + 729689.6 (T/K)^{-2}$	
	865 to 1201			$196.45 + 0.01830 T/K + 729689.6 (T/K)^{-2}$	
$K_2MoO_4(L)$	298.15 to 730.7	-1449.67	248.88	$113.50 + 0.09688 T/K + 729689.6 (T/K)^{-2}$	This work
	730.7 to 865			$-227.31 + 0.52473 T/K + 729689.6 (T/K)^{-2}$	
	865 to 1201			$196.45 + 0.01830 T/K + 729689.6 (T/K)^{-2}$	
	1201 to 1500			$204.67 + 0.01506 T/K$	

The standard enthalpy at 298.15 K ($\Delta_f H_{298}^\circ$) of $K_2MoO_4(I)$ was estimated as -1497.85 kJ mol⁻¹ as follows. Nelson et al. ⁶⁵ measured by calorimetry the enthalpy of dissolution of $K_2MoO_4(I)$ in a 10⁻³ M $OH_{(aq)}^-$ solution. These authors reported an enthalpy change of -3.97 kJ mol⁻¹ for the reaction $K_2MoO_4(I) \rightarrow 2K_{(aq)}^+ + MoO_4_{(aq)}^{2-}$. According to the FactSage databases, ⁶⁶

$\Delta_f H_{298}^\circ(\text{K}_{(\text{aq})}^+) = -251.97 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298}^\circ(\text{MoO}_4^{2-}_{(\text{aq})}) = -997.88 \text{ kJ mol}^{-1}$. There is no recommended value of $\Delta_f H_{298}^\circ$ for $\text{K}_2\text{MoO}_4(\text{I})$ in Barin's compilation tables. ⁶⁷ OQMD ^{68,69} reported an enthalpy of formation at 0 K of $-1575.70 \text{ kJ mol}^{-1}$ using DFT. The corresponding value given in Materials Project ⁷⁰ is $-1493.30 \text{ kJ mol}^{-1}$.

The standard entropy at 298.15 K (S_{298}°) of $\text{K}_2\text{MoO}_4(\text{I})$ was set to the value of $199.3 \text{ J mol}^{-1} \text{ K}^{-1}$ reported by Gavrichev et al. ⁴⁰ These authors derived this value by integration of $\int_0^{298.15 \text{ K}} \frac{C_P}{T} dT$ using their low-temperature heat capacity data obtained by adiabatic calorimetry. To our knowledge, this is the only experimental value available in the literature. S_{298}° was estimated by us using two different exchange reactions, for which $\Delta S = 0$ was assumed at 298.15 K. We derived a value of $182.79 \text{ J mol}^{-1} \text{ K}^{-1}$ from the exchange reaction $\text{Na}_2\text{MoO}_4(\text{I}) + \text{K}_2\text{CrO}_4(\text{I}) \rightarrow \text{K}_2\text{MoO}_4(\text{I}) + \text{Na}_2\text{CrO}_4(\text{I})$, and a value of $180.25 \text{ J mol}^{-1} \text{ K}^{-1}$ from the exchange reaction $\text{Na}_2\text{MoO}_4(\text{I}) + 2\text{KCl}_{(\text{sol})} \rightarrow \text{K}_2\text{MoO}_4(\text{I}) + 2\text{NaCl}_{(\text{sol})}$. The standard entropies at 298.15 K of $\text{Na}_2\text{MoO}_4(\text{I})$, $\text{K}_2\text{CrO}_4(\text{I})$ and $\text{Na}_2\text{CrO}_4(\text{I})$ were assessed by us in this work, and those of $\text{KCl}_{(\text{sol})}$ and $\text{NaCl}_{(\text{sol})}$ were taken from the FTsalt thermodynamic database. ⁶⁶ Our two derived S_{298}° values are very rough estimates. These are lower than the value reported by Gavrichev et al. ⁴⁰

The latter value, which was selected in this work, is probably somewhat too low since the experimental S_{298}° value of Gavrichev et al. ¹⁰¹ for Na_2MoO_4 was lower by about $10 \text{ J mol}^{-1} \text{ K}^{-1}$ than the values of ⁶⁷ and ⁹⁹ favored in this work.

To our knowledge, the low-temperature data of Gavrichev et al. ⁴⁰ are the only direct heat capacity measurements available for K_2MoO_4 . In the present work, the heat capacity (as a function of temperature) of K_2MoO_4 was assessed from the following exchange reactions, assuming that $\Delta C_P = 0$ at all temperatures : $\text{Na}_2\text{MoO}_4(\text{sol}) + 2\text{KCl}_{(\text{sol})} \rightarrow \text{K}_2\text{MoO}_4(\text{sol}) + 2\text{NaCl}_{(\text{sol})}$ for the solid phases (I, II, and III), and $\text{Na}_2\text{MoO}_4(\text{L}) + 2\text{KCl}_{(\text{L})} \rightarrow \text{K}_2\text{MoO}_4(\text{L}) + 2\text{NaCl}_{(\text{L})}$ for the pure liquid. The heat capacity of Na_2MoO_4 was evaluated in the present work, and those of KCl and NaCl were taken from the FTsalt database. ⁶⁶

In Figure 6, the calculated heat capacity of solid K_2MoO_4 at low temperatures is compared to three series of measurements (3, 4 and 6) conducted by Gavrichev et al. ⁴⁰ using DSC. These authors performed six different series of measurements at low temperatures : series 1 between 78.83 K and 215.59 K, series 2 between 132.27 K and 215.40 K, series 3 between 8.97 K and 75.08 K, series 4 between 174.38 K and 342.90 K, series 5 between 245 K and 257.31 K, and series 6 between 99.83

K and 116.16 K. Agreement from room temperature to 342.90 K (maximum temperature investigated by Gavrichev et al.⁴⁰) is satisfactory.

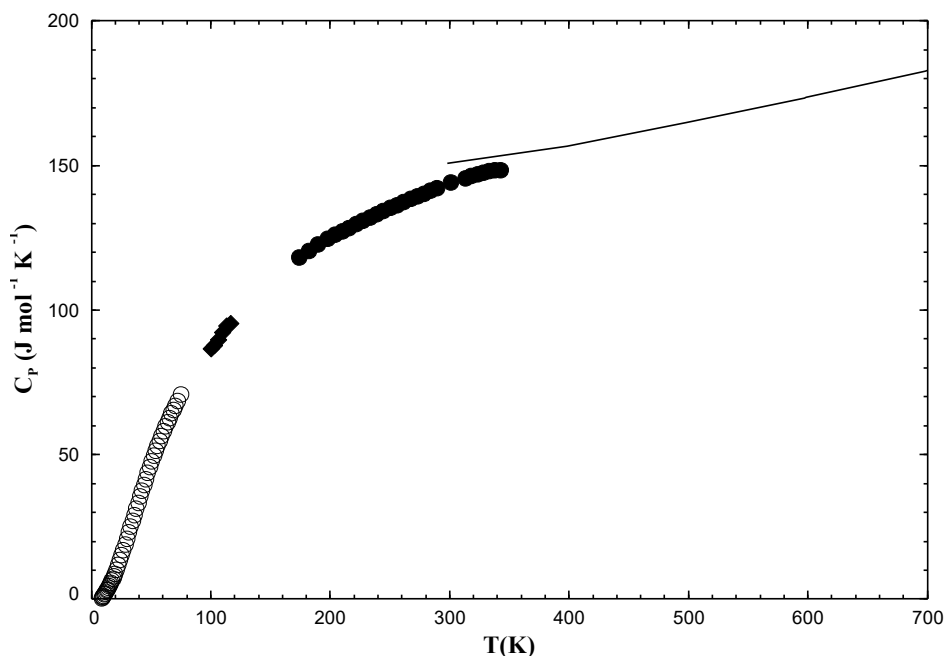


Figure 6 : Calculated heat capacity at low temperatures for $\text{K}_2\text{MoO}_4(\text{I})$. Experimental data from ⁴⁰ (series 3 : \circ , series 4 : \bullet , and series 6 : \blacklozenge).

4.5 Sodium tungstate

4.5.1 Transition temperature (T_{trs}) and enthalpy change (ΔH_{trs}) of solid-solid transitions (I \rightarrow II and II \rightarrow III) for Na_2WO_4

The temperatures and enthalpy changes for the solid-solid transitions (I \rightarrow II and II \rightarrow III) of Na_2WO_4 were measured by DSC in the present work. These measurements along with all data collected from the literature are displayed in Tables 23 and 24, respectively. Our experimental DSC thermogram is displayed in the Supporting Information (Figure S4).

Table 23 : Transition temperature and enthalpy change of transition I→II for Na₂WO₄

$T_{\text{trs}}(\text{I} \rightarrow \text{II})$ (°C)	$\Delta H_{\text{trs}}(\text{I} \rightarrow \text{II})$ (kJ mol ⁻¹)	Experimental Method	Reference
-	28.93	DSC (2 nd heating) at 10 °C/min	This work
-	28.66	DSC (3 rd heating) at 10 °C/min	This work
564‡	-	Cooling curves	46
587	-	Cooling curves*	106
587.6	30.851	DTA	107
579‡	39.790‡	Heating or cooling curves	74
588	31.380 ± 0.146	DTA** at 1 °C/min	86
591	34.434	DTA	53
585.9 ± 3	31.506 ± 0.502	Calorimetry, drop method	54
587.9	-	DSC (cooling) at 0.3 °C/min	36
559.9‡	-	Raman spectroscopy	33
-	3.3‡	Thermal analysis (DSC) 8-10°C/min	108
589	-	DSC (heating) at 0.1 °C/min	45
588.3 ± 3.1	31.5 ± 5.9***	Weighted average	This work

* Cooling rates were not provided, but it was mentioned that various (slow) cooling rates were used.

** Enthalpy changes were measured upon cooling while temperatures were measured upon heating.

*** See explanation in text

‡ Outlier

Table 24 : Transition temperature and enthalpy change of transition II→III for Na₂WO₄

$T_{\text{trs}}(\text{II} \rightarrow \text{III})$ (°C)	$\Delta H_{\text{trs}}(\text{II} \rightarrow \text{III})$ (kJ mol ⁻¹)	Experimental Method	Reference
-	-	DSC (2 nd heating) at 10 °C/min	This work

-	-	DSC (3 rd heating) at 10 °C/min	This work
564-588	-	Cooling curves	46
591	-	Cooling curves*	106
588.8	4.113 ± 0.015	DTA	107
589	4.142 ± 0.146	DTA at 1 °C/min	86
589.9	-	DSC (cooling) at 0.3 °C/min	36
591	-	DSC (heating) at 0.1 °C/min	45

* Cooling rates were not provided, but it was mentioned that various (slow) cooling rates were used.

4.5.2 Temperature (T_{fus}) and enthalpy of fusion (ΔH_{fus}) for Na_2WO_4

The properties of fusion (temperature and enthalpy change) were measured by.^{36, 46, 53, 54, 62, 86, 97, 106-109} The heat of fusion was obtained by DTA^{53, 86, 107, 108} and drop calorimetry.⁵⁴ All experimental data collected from the literature and our own DSC measurements are compiled in Table 25.

Table 25 : Transition temperature and enthalpy of fusion for Na_2WO_4

T_{fus} (III→L) (°C)	ΔH_{fus} (III→L) (kJ mol ⁻¹)	Experimental Method	Reference
690.8	24.47	DSC (2 nd heating) at 10 °C/min	This work
690.9	23.85	DSC (3 rd heating) at 10 °C/min	This work
698	-	Cooling curves	46
694	-	Cooling curves	106
695.5	23.799 ± 0.015	DTA	107
698	-	Visual-polythermal analysis	109
696	31.254 ± 0.146	DTA at 1 °C/min	86
698	31.464	DTA	53
693	-	Visual-polythermal analysis	62
689	-	Thermal analysis	97
693.9 ± 2	27.865 ± 0.586	Calorimetry, drop method	54
693.9	-	DSC (cooling) at 0.3 °C/min	36

695.9 ± 2	$34 \pm 3.5\ddagger$	Thermal analysis (DTA) 8-10 °C/min	¹⁰⁸
694.2 ± 5.6	27.0 ± 6.6	Weighted average	This work

‡ Outlier

4.5.3 Recommended thermodynamic data for sodium tungstate Na₂WO₄

Our selected thermodynamic data ($\Delta_f H_{298}^\circ$, S_{298}° , and C_p) for sodium tungstate (Na₂WO₄) are given in Table 26.

Table 26 : Selected thermodynamic properties of Na₂WO₄

Phase	T Range (K)	$\Delta_f H_{298}^\circ$ (kJ mol ⁻¹)	S_{298}° (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	Reference
Na ₂ WO ₄ (I)	298.15	-1544.73			110
			161.08		111
	298.15 to 861.5			$130.18 + 0.06734 T/K$	54
Na ₂ WO ₄ (II)	298.15	-1513.26	197.61		This work
	298.15 to 861.5			$130.18 + 0.06734 T/K$	54
	861.5 to 967.4			$-29.72 + 0.25581 T/K$	
Na ₂ WO ₄ (L)	298.15	-1486.31	225.47		This work
	298.15 to 861.5			$130.18 + 0.06734 T/K$	54
	861.5 to 967.4			$-29.72 + 0.25581 T/K$	
	967.4 to 2000			216.19	

Various studies were conducted to identify the number of solid-solid transitions. Some authors reported a single solid-solid transition^{33, 53, 54, 74, 108} while others reported two such transitions.^{36, 45, 86, 106, 107}

Denielou et al.⁵⁴ used drop calorimetry to measure heat contents ($H_T - H_{273}$) whereas Riccardi and Sinistri⁵³ performed DTA measurements; both studies reported a single solid-solid transition (see Table 23). The DSC analyses of Bottelberghs and van Buren³⁶ were able to separate the peaks corresponding to the I→II and II→III transitions using a very low heating rate of 0.3 °C/min. They estimated the temperature range of stability of the phase II to be only about 2 °C. According to Bottelberghs and van Buren,³⁶ the previous studies did not observe the II→III transition because their calorimetric apparatuses were not calibrated with Zn, thus preventing them from measuring quantitatively and separately all solid-solid transitions.

Goranson and Kracek ¹⁰⁷ observed large overheating and undercooling effects for the II→III transition on their differential heating and cooling curves; they reported a difference of only 1.2 °C between their temperatures for the I→II and II→III transitions. Similarly, the DSC measurements of Hämmer and Höppe ⁴⁵ at a heating rate of 0.1 °C/min showed these two solid-solid transitions, with a temperature difference of only 2 °C.

Our DSC measurements for Na₂WO₄ were performed at a heating/cooling rate of 10 °C/min. One solid-solid transition was observed upon heating whereas two different solid-solid transitions were observed upon cooling. The presence of two exothermic events in our DSC cooling curves indicates that both phase transitions were reversible. ⁴⁵

For the temperature of the I→II transition, the value of Hare, ⁷⁴ which is relatively low compared to all other available data, was discarded. Also, the value of Suponitskiy et al. ¹⁰⁸ for the enthalpy change of the I→II transition was not considered since it is substantially different from all other measurements (see Table 23).

Our weighted averages of the temperatures for the I→II and II→III transitions are 588.3 °C and 589.6 °C (see Tables 23 and 24), respectively, with a temperature difference of only 1.3 °C. Hence, only two phases for Na₂WO₄ were considered in the present work: the low-temperature phase I and the high-temperature phase III (which was renamed II for the sake of clarity, as seen in Table 26). Nolte and Kordes, ⁸⁶ and Goranson and Kracek ¹⁰⁷ are the only authors who were able to measure the enthalpy changes of the I→II and II→III transitions. Our selected enthalpy change for the I→II transition (where the notation “II” now refers to the high-temperature phase III) is the sum of the two enthalpy changes for the I→II and II→III transitions reported in ⁸⁶ and ¹⁰⁷ (A weighted average of these two series of data was used).

For both Na₂WO₄ and Na₂MoO₄, the enthalpy change of the I→II transition is higher than the enthalpy of fusion. Therefore, for both compounds, the entropy change of the I→II transition exceeds the entropy of fusion. For Na₂WO₄, Goranson and Kracek ¹⁰⁷ estimated the volume changes related to the I→II transition and to the fusion using their calorimetric data and the Clausius-Clapeyron relation. Based on these values (see Table 27), the molar volume change associated with the I→II transition is larger than the molar volume change upon melting. This explains the ranking of the corresponding entropy changes. It is very likely that the same phenomenon occurs for Na₂MoO₄.

Table 27 : Volume change of Na₂WO₄

Transition	Volume change (cm ³ g ⁻¹)	Volume change (cm ³ mol ⁻¹)	Reference
Na ₂ WO ₄ (I→II)	0.035	10.284	¹⁰⁷
Na ₂ WO ₄ (III→L)	0.018	5.289	¹⁰⁷

The standard enthalpy at 298.15 K ($\Delta_f H_{298}^\circ$) of Na₂WO₄(I) was estimated by JANAF ¹¹⁰ from the reaction $\text{H}_2\text{WO}_4(\text{sol}) + 2 \text{NaCl}(\text{sol}) = \text{Na}_2\text{WO}_4(\text{I}) + 2 \text{HCl}(\text{aq.}, 12.73 \text{ H}_2\text{O})$, using $\Delta_f H_{298}^\circ(\text{H}_2\text{WO}_4(\text{sol})) = -1131.77 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298}^\circ(\text{NaCl}(\text{sol})) = -411.12 \text{ kJ mol}^{-1}$ both taken from ¹¹⁰, the heat of reaction $\Delta_r H_{303}^\circ = 81.34 \pm 0.33 \text{ kJ mol}^{-1}$ measured by Koehler et al., ¹⁰⁰ and $\Delta_f H_{298}^\circ(\text{HCl}(\text{aq.})) = -74.84 \pm 62.76 \text{ kJ mol}^{-1}$ provided in. ¹¹²

The enthalpy change at 298.15 K of the reaction $\text{W}(\text{sol}) + 2 \text{NaOH}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) = \text{Na}_2\text{WO}_4(\text{aq}) + 3 \text{H}_2(\text{g})$ was measured by calorimetry as $-29.29 \pm 6.28 \text{ kJ mol}^{-1}$. ¹¹³ The heat of solution for the reaction $\text{Na}_2\text{WO}_4(\text{I}) = \text{Na}_2\text{WO}_4(\text{aq})$ was then measured as $-7.11 \pm 0.42 \text{ kJ mol}^{-1}$, which finally permitted to derive a value of $-1541.39 \text{ kJ mol}^{-1}$ for $\Delta_f H_{298}^\circ(\text{Na}_2\text{WO}_4(\text{I}))$. This latter value is close to the value of $-1544.73 \text{ kJ mol}^{-1}$ recommended by JANAF. ¹¹⁰

Using a cycle of calorimetric reactions, Koehler et al. ¹⁰⁰ estimated $\Delta_f H_{298}^\circ(\text{Na}_2\text{WO}_4(\text{I}))$ as $-1586.57 \text{ kJ mol}^{-1}$.

Graham and Hepler ¹¹⁴ measured by calorimetry at 298.15 K the enthalpy of dissolution of Na₂WO₄(I) in small concentrations of NaOH or in 0.005-0.01 M NH₄OH, according to the reaction $\text{Na}_2\text{WO}_4(\text{I}) \rightarrow 2\text{Na}^+(\text{aq}) + \text{WO}_4^{2-}(\text{aq})$. From their experimental enthalpy change for the reaction $\text{H}_2\text{WO}_4(\text{sol}) + 2 \text{OH}^-(\text{aq}) = \text{WO}_4^{2-}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$ and the standard enthalpies at 298.15 K of H₂WO₄(sol), OH⁻ and H₂O taken from, ¹¹⁵ they first estimated $\Delta_f H_{298}^\circ(\text{WO}_4^{2-}(\text{aq}))$. The obtained value was consistent with that of the Bureau of Standards. ¹¹⁵ Then, from the latter value, the standard enthalpy at 298.15 K of Na⁺(aq) provided by ¹¹⁵ and their measured enthalpy of dissolution of Na₂WO₄(I) ($-6.69 \pm 0.42 \text{ kJ mol}^{-1}$), they assessed $\Delta_f H_{298}^\circ(\text{Na}_2\text{WO}_4(\text{I}))$ as $-1588.25 \text{ kJ mol}^{-1}$.

Finally, the $\Delta_f H_{298}^\circ$ value recommended by JANAF ¹¹⁰ was selected in this work. Indeed, according to JANAF, ¹¹⁰ Koehler et al. ¹⁰⁰ and Graham and Hepler ¹¹⁴ used an erroneous value of $-1172.36 \text{ kJ mol}^{-1}$ for $\Delta_f H_{298}^\circ(\text{H}_2\text{WO}_4(\text{sol}))$. Also, note that U.S. Nat. Bur. Stand. Circ. 500 ¹¹⁵ reported a value of $-1652.68 \text{ kJ mol}^{-1}$ for $\Delta_f H_{298}^\circ(\text{Na}_2\text{WO}_4(\text{I}))$. This value was derived from the experimental heat of reaction of tungsten powder using an excess of Na₂O₂. As mentioned in, ¹¹⁰ this approach

is most likely wrong owing to the possible formation of tungstate and complexes of peroxytungstate.

The standard enthalpy at 298.15 K of Na₂WO₄(I) was estimated by us using the method proposed by Hisham and Benson.¹¹⁶ These authors derived equations of the type $\frac{1}{a}\Delta_f H_{298}^\circ(M_a X_b) = m\Delta_f H_{298}^\circ(MCl) + \frac{1-m}{2}\Delta_f H_{298}^\circ(M_2O) + C$, where m and C are two constants, and $\Delta_f H_{298}^\circ$ refers to the standard enthalpy at 298.15 K of the corresponding solid compound. They selected the corresponding chloride and oxide of a metal M as reference compounds since, for the majority of metals, the chloride and oxide values are known with good accuracy. For the alkali tungstates, Hisham and Benson¹¹⁶ obtained m = 2.93 and C = -426.35 kJ mol⁻¹. Using the $\Delta_f H_{298}^\circ$ values for solid NaCl and Na₂O from the FactSage thermodynamic databases,⁶⁶ $\Delta_f H_{298}^\circ(\text{Na}_2\text{WO}_4(\text{I}))$ was assessed as -1554.87 kJ mol⁻¹, which is reasonably close to the value recommended by JANAF¹¹⁰ and selected in the present work. OQMD^{68, 69} reported an enthalpy of formation at 0 K of -1637.84 kJ mol⁻¹ using DFT. The corresponding value given in Materials Project⁷⁰ is -1500.06 kJ mol⁻¹.

Using calorimetry, King and Weller¹¹¹ performed low-temperature heat capacity measurements for Na₂WO₄(I), and derived from them a value of 161.08 J mol⁻¹ K⁻¹ for the standard entropy at 298.15 K (S_{298}°). (The temperature range from 0 K to 51 K was extrapolated using the Einstein and Debye functions.) This value, which is recommended by JANAF,¹¹⁰ was selected in the present work.

Na₂WO₄ was studied by Denielou et al.,⁵⁴ using the same experimental technique that was previously discussed in detail for Na₂CrO₄ and Na₂MoO₄. These authors provided fits (as a function of temperature) for their heat content measurements ($H_T - H_{273}$). For Na₂WO₄(I), based on fourteen measurements between 345 K and 849 K, $H_T - H_{273} = 3.367 \times 10^{-5}T^2 + 1.302 \times 10^{-1}T - 38.58$ kJ mol⁻¹ (0.4 %, empirical standard variation of 0.03 kJ). This fit was assumed to be valid from 298.15 K to our selected temperature of 861.5 K for the I→II transition.

For Na₂WO₄(II), based on nine measurements between 862 K and 957 K, $H_T - H_{273} = 1.279 \times 10^{-4}T^2 - 2.972 \times 10^{-2}T + 60.75$ kJ mol⁻¹ (0.4 %, empirical standard variation of 0.05 kJ). This fit was assumed to be valid from 861.5 K until our selected temperature of fusion of 967.4 K.

For Na₂MoO₄(L), based on twelve measurements above 992 K, $H_T - H_{273} = 2.162 \times 10^{-1}T - 29.61$ kJ mol⁻¹ (0.14 %, empirical standard variation of 0.08 kJ).⁵⁴

In this work, the heat capacity expression (as a function of temperature) for Na₂WO₄ was selected in order to reproduce the heat content measurements ($H_T - H_{273}$) of Denielou et al.⁵⁴ Calculations

are compared to the available data in Figure 7. Also, the calculated heat capacity is shown along with the low-temperature measurements of King and Weller¹¹¹ in Figure 8. At room temperature, agreement is reasonable.

In Figure 7, the black full lines represent our final calculations while the red dashed line refers to $H_T - H_{273}$ heat contents obtained from the fit of the room temperature C_p data of¹¹¹ displayed in Figure 8. An average deviation of about 4 kJ mol⁻¹ is calculated for the red dashed line, which is significantly higher than the experimental error of 0.03 kJ mol⁻¹ reported by⁵⁴. This lends support to our final calculations shown in Figures 7 and 8.

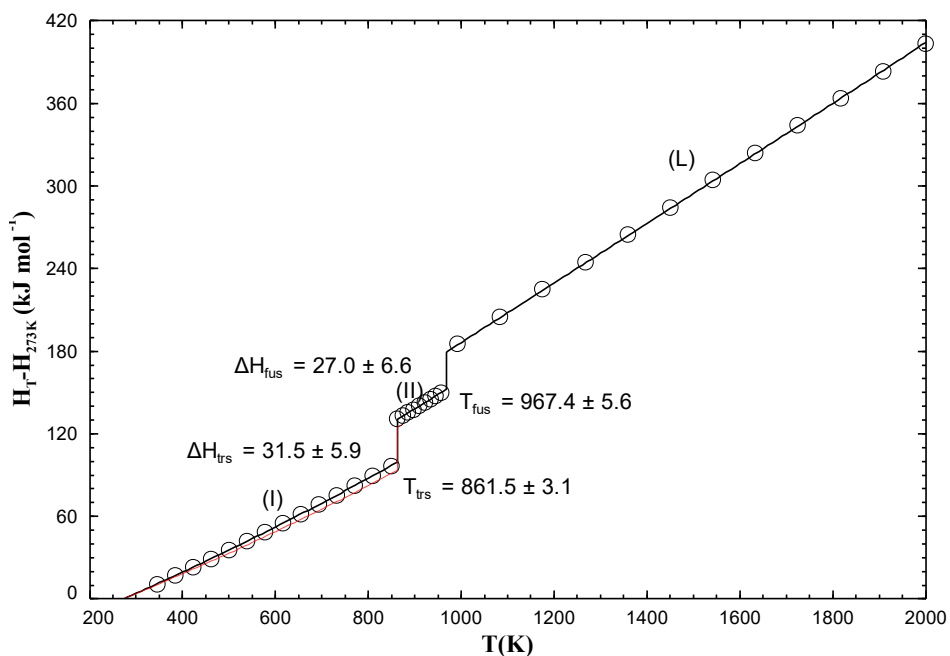


Figure 7 : Calculated heat content $H_T - H_{273}$ for Na_2WO_4 (enthalpies of transition are the weighted average of all available data presented in tables 23 and 25). Experimental data from⁵⁴ (○). Red dashed line : $H_T - H_{273}$ fit of low-temperature heat capacity data shown in Figure 8.

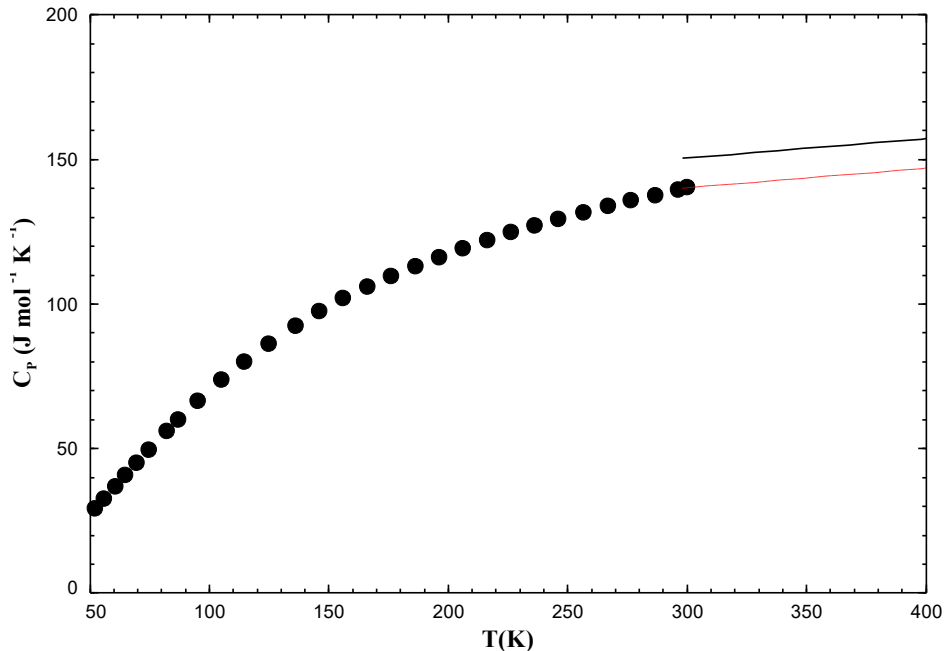


Figure 8 : Calculated heat capacity at low temperatures for Na₂WO₄(I). Experimental data from ¹¹¹ (●). Red dashed line : best linear fit of room temperature C_P data.

4.6 Potassium tungstate

4.6.1 Transition temperature (T_{trs}) and enthalpy change (ΔH_{trs}) of solid-solid transitions (I→II and II→III) for K₂WO₄

The temperatures and enthalpy changes for the solid-solid transitions (I→II and II→III) of K₂WO₄ were measured by DSC in the present work. These measurements along with all data from the literature are shown in Tables 28 and 29, respectively. Our experimental DSC thermogram is displayed in the Supporting Information (Figure S5). Some authors reported a single solid-solid transition ^{86, 117} while others reported two such transitions. ^{42, 53, 91, 108} Our DSC measurements at a heating/cooling rate of 10°C/min confirmed that K₂WO₄ exhibits two different solid-solid transitions.

Table 28 : Transition temperature and enthalpy change of transition I→II for K₂WO₄

$T_{\text{trs}}(\text{I} \rightarrow \text{II})$ (°C)	$\Delta H_{\text{trs}}(\text{I} \rightarrow \text{II})$ (kJ mol ⁻¹)	Experimental Method	Reference
362.7	9.82	DSC (2 nd heating) at 10 °C/min	This work
361.7	9.84	DSC (3 rd heating) at 10 °C/min	This work
358	-	Cooling curves	117
350‡	9.121 ± 0.146	DTA at 1 °C/min	86
381‡	11.464	DTA	53
370	-	DTA at 5 °C/min	91
370	-	XRD*	42
-	12	Thermal analysis (DTA) 8-10 °C/min	108
364.1 ± 9.6	10.3 ± 2.2	Weighted average	This work

* A high temperature focusing Guinier camera from Nonius was used with a calibrated thermocouple. The estimated error is about ± 10 °C.

‡ Outlier

Table 29 : Transition temperature and enthalpy change of transition II→III for K₂WO₄

$T_{\text{trs}}(\text{II} \rightarrow \text{III})$ (°C)	$\Delta H_{\text{trs}}(\text{II} \rightarrow \text{III})$ (kJ mol ⁻¹)	Experimental Method	Reference
461.1	1.031	DSC (2 nd heating) at 10 °C/min	This work
461.3	1.001	DSC (3 rd heating) at 10 °C/min	This work
456	1.046	DTA	53
455	-	DTA at 5 °C/min	91
435‡	-	XRD*	42
-	1.2	Thermal analysis (DTA) 8-10 °C/min	108

458.4 ± 5.7	1.1 ± 0.2	Weighted average	This work
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* A high temperature focusing Guinier camera from Nonius was used with a calibrated thermocouple. The estimated error is about ± 10 °C.

‡ Outlier

4.6.2 Temperature (T_{fus}) and enthalpy of fusion (ΔH_{fus}) for K_2WO_4

The properties of fusion (temperature and enthalpy change) were determined by.^{53, 62, 73, 86, 97, 118, 119} All experimental data from the literature and our own DSC measurements are presented in Table 30.

Table 30 : Transition temperature and enthalpy of fusion for K_2WO_4

T_{fus} (III→L) (°C)	ΔH_{fus} (III→L) (kJ mol ⁻¹)	Experimental Method	Reference
928.2	32.47	DSC (2 nd heating) at 10 °C/min	This work
927.7	32.57	DSC (3 rd heating) at 10 °C/min	This work
894‡	-	Cooling curves	73
926	-	Visual-polythermal analysis	118
926	-	Visual-polythermal analysis	119
928	31.087 ± 0.146	DTA at 1 °C/min	86
923	30.711	DTA	53
919‡	-	Visual-polythermal analysis	62
926	-	Thermal analysis	97
926.5 ± 3.3	32.0 ± 1.7	Weighted average	This work

‡ Outlier

4.6.3 Recommended thermodynamic data for potassium tungstate K_2WO_4

Our selected thermodynamic data ($\Delta_f H_{298}^\circ$, S_{298}° , and C_p) for potassium tungstate (K_2WO_4) are given in Table 31.

Table 31 : Selected thermodynamic properties of K₂WO₄

Phase	T Range (K)	$\Delta_f H_{298}^\circ$ (kJ mol ⁻¹)	S_{298}° (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	Reference
K ₂ WO ₄ (I)	298.15	-1581.60	175.81		(FactSage, SGPS database ⁶⁶)
	298.15 to 637.3			113.39 + 0.12552 T/K	
K ₂ WO ₄ (II)	298.15	-1571.33	191.92		This work
	298.15 to 637.3			113.39 + 0.12552 T/K	(FactSage, SGPS database ⁶⁶)
	637.3 to 731.5			194.56	
K ₂ WO ₄ (III)	298.15	-1570.28	193.36		This work
	298.15 to 637.3			113.39 + 0.12552 T/K	(FactSage, SGPS database ⁶⁶)
	637.3 to 1199.6			194.56	
K ₂ WO ₄ (L)	298.15	-1538.30	220.02		This work
	298.15 to 637.3			113.39 + 0.12552 T/K	(FactSage, SGPS database ⁶⁶)
	637.3 to 1199.6			194.56	
	1199.6 to 2000			213.38	

The standard enthalpy at 298.15 K ($\Delta_f H_{298}^\circ$) was taken directly from the SGPS database in FactSage. ⁶⁶ Indeed, this value (-1581.6 kJ mol⁻¹) is close to the value of -1574.0 kJ mol⁻¹ assessed using the equation of Hisham and Benson ¹¹⁶ with an approach similar to that described previously for Na₂WO₄. The validity of this equation was confirmed by us for the compounds Na₂CrO₄, K₂CrO₄, Na₂MoO₄ and K₂MoO₄, for which there was good agreement between the estimated $\Delta_f H_{298}^\circ$ values and our selected values based on experimental data from the literature. For K₂WO₄, OQMD ^{68, 69} reported an enthalpy of formation at 0 K of -1645.27 kJ mol⁻¹ using DFT. The corresponding value given in Materials Project ⁷⁰ is -1528.42 kJ mol⁻¹.

The standard entropy at 298.15 K (S_{298}°) of K₂WO₄(I) was taken directly from the SGPS database in FactSage ⁶⁶ since no other values were available in the literature. Also, S_{298}° was roughly estimated from the exchange reactions Na₂WO₄(I) + K₂CrO₄(I) → K₂WO₄(I) + Na₂CrO₄(I) and Na₂WO₄(I) + 2 KCl_(sol) → K₂WO₄(I) + 2 NaCl_(sol), for which ΔS was assumed to be null at 298.15 K. The corresponding estimates are 184.46 J mol⁻¹ K⁻¹ and 181.92 J mol⁻¹ K⁻¹, respectively, which compares reasonably well to our selected value of 175.81 J mol⁻¹ K⁻¹.

To our knowledge, no experimental data for the heat capacity of K_2WO_4 are published. Therefore, the heat capacity expression (as a function of temperature) for this compound was taken directly from the SGPS database of FactSage.⁶⁶

4.7 Summary table of recommended values

Table 32 provides a summary of all transition temperatures and enthalpies of transition estimated in the present work, along with their assessed uncertainties.

Table 32 : Summary table of recommended values

Transition	T_{trs} (°C)	$U(T_{\text{trs}})$ (°C)	ΔH_{trs} (kJ mol ⁻¹)	$U(\Delta H_{\text{trs}})$ (kJ mol ⁻¹)
Na₂CrO₄(I→II)	419.1	2.7	9.6	0.6
Na₂CrO₄(II→L)	793.3	3.2	24.3	0.9
K₂CrO₄(I→II)	669.2	7.1	7.0	0.5
K₂CrO₄(II→L)	975.9	9.9	33.1	1.8
Na₂MoO₄(I→II)	457.6	3.7	23.1	4.9
Na₂MoO₄(II→III)	591.8	2.5	1.9	0.3
Na₂MoO₄(III→IV)	640.6	3.4	8.2	0.4
Na₂MoO₄(IV→L)	687.1	3.5	20.4	2.5
K₂MoO₄(I→II)	323.5	3.8	10.6	2.9
K₂MoO₄(II→III)	454.7	3.9	1.0	0.1
K₂MoO₄(III→L)	927.8	5.9	36.6	5.0
Na₂WO₄(I→II)	588.3	3.1	31.5	5.9
Na₂WO₄(II→L)	694.2	5.6	27.0	6.6
K₂WO₄(I→II)	364.1	9.6	10.3	2.2
K₂WO₄(II→III)	458.4	5.7	1.1	0.2
K₂WO₄(III→L)	926.5	3.3	32.0	1.7

5. Conclusions

In this work, thermodynamic properties (standard enthalpy at 298.15 K, standard entropy at 298.15 K, heat capacity as a function of temperature) were selected for all condensed phases of the compounds Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 and K_2WO_4 , based on a critical analysis of all available experimental data from the literature. In addition, for the six compounds, the temperatures and enthalpy changes of all solid-solid transitions and of fusion were measured by DSC. Those data were also considered for our selection of the thermodynamic properties. Crystal structures and space groups were collected from the literature for all phases of the six compounds. High-temperature XRD measurements permitted us to conclude that K_2MoO_4 displays three phases instead of the four reported in several publications.

The present work is the first step towards the development of a thermodynamic model for the Na^+ , $\text{K}^+ // \text{Cl}^-$, SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$, O^{2-} system that is relevant in the high temperature corrosion of equipment such as heat-transfer tubes. A critical evaluation of the thermodynamic properties of the compounds $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{W}_2\text{O}_7$ and $\text{K}_2\text{W}_2\text{O}_7$ will be described in a subsequent paper. These compounds need to be considered since reactions of the type $2 \text{A}_2\text{MO}_4 \rightleftharpoons \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$ (where $\text{A} = \text{Na}, \text{K}$ and $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) may partly occur. Through phase equilibria calculations (which will avoid a tedious and costly trial and error experimental approach), the developed thermodynamic model will permit us to better understand high temperature corrosion phenomena in the temperature range 600-950 °C. The developed thermodynamic model will also enable a better investigation of the chemistry of ash deposits and heat exchanger alloys since the combined ash/gas/alloy chemistry controls the melting behaviour of ashes.

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Supporting information

Supporting information to this article can be found online at

Conflict of Interest

The authors have no conflict to disclose.

Data availability

The data that supports the findings of this study are available within the article [and its supplementary material].

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