



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Thermodynamic Model for High Temperature Corrosion Applications: The (NaCl + Na2CO3 + Na2SO4 + Na2S2O7 + Na2CrO4 + Na2Cr2O7 + Na2MoO4 + Na2Mo2O7 + Na2O + KCl + K2CO3 + K2SO4 + K2S2O7 + K2CrO4 + K2Cr2O7 + K2MoO4 + K2Mo2O7 + K2O) System

Benalia, Sara; Tesfaye, Fiseha; Lindberg, Daniel; Hupa, Leena; Chartrand, Patrice; Robelin, Christian

Published in: Industrial & Engineering Chemistry Research

DOI: 10.1021/acs.iecr.3c02295

E-pub ahead of print: 04/12/2023

Document Version Accepted author manuscript

Document License CC BY-NC-ND

Link to publication

Please cite the original version:

Benalia, S., Tesfaye, F., Lindberg, D., Hupa, L., Chartrand, P., & Robelin, C. (2023). Thermodynamic Model for High Temperature Corrosion Applications: The (NaCl + Na2CO3 + Na2SO4 + Na2SO7 + Na2CrO4 + Na2Cr2O7 + Na2MoO4 + Na2Mo2O7 + Na2O + KCl + K2CO3 + K2SO4 + K2S2O7 + K2CrO4 + K2Cr2O7 + K2MoO4 + K2Mo2O7 + K2O) System. *Industrial & Engineering Chemistry Research*, 1-31. Advance online publication. https://doi.org/10.1021/acs.iecr.3c02295

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

A Thermodynamic Model for High Temperature Corrosion Applications : The (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂MoO₄ + Na₂Mo₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇ + K₂O) System

Sara Benalia^{a,b}, Fiseha Tesfaye^{b,c}, Daniel Lindberg^d, Leena Hupa^b, Patrice Chartrand^a, Christian Robelin^{a,*}

^a Centre for Research in Computational Thermochemistry (CRCT), Department of Chemical Engineering, Polytechnique Montréal, Box 6079, Station Downtown, Montréal (Quebec), Canada, H3C 3A7

^b Johan Gadolin Process Chemistry Centre, Laboratory of Molecular Science and Engineering, Åbo Akademi University, Henrikinkatu 2, FI-20500 Turku, Finland

^c Metso Outotec Metals Oy, Rauhalanpuisto 9, PO Box 1000, FI-02231 Espoo, Finland

^d Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, FI-00076 Aalto, Finland

Abstract

A thermodynamic model has been developed for the condensed phases of the salt system $(NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7 + Na_2MoO_4 + Na_2Mo_2O_7 + Na_2O + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7 + K_2CrO_4 + K_2Cr_2O_7 + K_2MoO_4 + K_2Mo_2O_7 + K_2O)$ (diluted in free oxides), which is most often involved in combustion processes for energy production. This model is relevant in particular for the solid deposits formed in steel and stainless steel installations containing Ni, Cr, Mo, W, and V as alloying elements, and permits the accurate prediction of thermodynamic properties and phase equilibria in the multicomponent system. The $(NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7 + Na_2O + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7 + K_2CrO_4 + K_2Cr_2O_7 + K_2O)$ sub-system was critically evaluated in previous papers. In the present work, Na₂MoO₄, K₂MoO₄, Na₂Mo₂O₇, and K₂Mo₂O₇ have been added to the previously developed thermodynamic model. The available phase diagram and thermodynamic data have been critically evaluated, and model parameters have been obtained. The Modified Quasichemical Model in the Quadruplet Approximation was used for both the liquid solution and the high-temperature hexagonal solid solution $(Na_2CO_3 + Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4 + K_2CO_3 + K_2SO_4 + K_2CrO_4 + [K_2MoO_4])$, whereas the Compound Energy Formalism (CEF) was used for all other solid solutions.

Due to the lack of data, several common-ion binary sub-systems have been investigated in this work at different compositions by DSC-TGA. In addition, the non-stoichiometric molybdenum-glaserite phase has been studied at the composition ($35 \text{ mol}\% \text{ Na}_2\text{MoO}_4 + 65 \text{ mol}\% \text{ K}_2\text{MoO}_4$) using SEM-EDS and DSC-TGA, after annealing at 400°C for four weeks.

Keywords: Thermodynamic modeling; Phase diagrams; Alkali molybdates; Alkali dimolybdates; DSC-TGA

*Corresponding author (E-mail address: christian.robelin@polymtl.ca)

1. Introduction

Hot corrosion in steels and stainless steels consisting of the alloying elements Ni, Cr, Mo, W, and V refers to accelerated oxidation occurring at high temperatures (from 600 to 950°C) ¹⁻³ in the presence of combustion gases (N₂, CO₂, CO, O₂, H₂O, etc.) containing contaminants (SO₂, Cl₂, S₂, HCl, etc.), and corrosive products (Na₂O, K₂O, NaOH, KOH, NaCl, KCl, etc.). ^{4, 5} Typical corrosion temperatures for some combustion processes, such

as black liquor combustion, are of the order of 500°C. The threshold for these temperatures depends on the lowest melting temperature of the ashes produced.

Hot corrosion is an accelerated attack associated with corrosive deposits accumulating on the plant walls, specifically NaCl, KCl, Na₂CO₃, K₂CO₃, Na₂SO₄, K₂SO₄,^{1, 4, 6-8} Na₂CrO₄ and K₂CrO₄ ^{4, 9, 10} salts. Further salts are known to promote corrosion, such as Na₂MoO₄ and K₂MoO₄ ^{4, 10, 11} in the solid or liquid form and can dissolve into the previously mentioned salts.

According to Misra's investigation, 12 MoO₃ flux created at the interface between the metal and the scale initiates catastrophic corrosion in molybdenum-containing superalloys. 12 The transformation of Na₂SO₄ into Na₂CrO₄ can occur long before the onset of catastrophic corrosion, which is accompanied by the conversion of Na₂CrO₄ to Na₂MoO₄. A mixture of Na₂MoO₄ and MoO₃ has been attributed to this kind of catastrophic corrosion. 12

Peters et al. ¹³ previously reported the oxidation of Na₂SO₄/Na₂MoO₄-coated samples, for which a Na₂SO₄-coated (Ni-15% Cr) alloy exhibited a severe corrosion behavior in the same reaction chamber as the Ni-15Cr-Mo alloys. That is, MoO₃ was dissolving in the salt layer and was then carried into the vapor phase according to the reaction Na₂SO₄ + MoO₃ = Na₂MoO₄ + SO₃.

An accurate thermodynamic model is available for the condensed phases of the (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂O) system (diluted in free oxides). The chromium-free version was originally developed by Lindberg et al. ^{14, 15} and then extended in our previous study. ¹⁶ The present paper describes the addition of molybdates (Na₂MoO₄ and K₂MoO₄) and dimolybdates (Na₂Mo₂O₇ and K₂Mo₂O₇) to our existing model. In our previous works, ^{4, 17} an assessment of the thermodynamic properties (standard enthalpy of formation $\Delta H^{\circ}_{298,15 \text{ K}}$ from the elements in their stable standard state at 298.15K and 1 atm, absolute (third law) entropy $S^{\circ}_{298,15 \text{ K}}$ referenced at 298.15K and 1 atm, and heat capacity *C*_P as a function of temperature) was performed for Na₂MoO₄, K₂MoO₄, Na₂Mo₂O₇ and K₂Mo₂O₇. Also, extensive information on the crystal structures of all allotropes of these four compounds was obtained from the literature, making it easier to identify possible solid solutions forming with other considered salts.

In the liquid solution of the $(NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7)$

+ Na₂MoO₄ + Na₂Mo₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇ + K₂O) system described in the present article, free oxides are present in dilute amounts since reactions of the type 2 A₂MO₄ = A₂M₂O₇ + A₂O (where A = Na, K and M = Cr, Mo) are very limited up to above the liquidus temperatures. ¹⁷

The developed thermodynamic model has been calibrated using the CALPHAD approach (CALculation of PHAse Diagrams), based on the available thermodynamic and phase equilibrium data from the literature, and also on our differential scanning calorimetry

(DSC)-thermogravimetric analysis (TGA) measurements at several compositions in the following common-ion binary sub-systems : $(Na_2CO_3 + Na_2MoO_4)$, $(Na_2SO_4 + Na_2MoO_4)$, $(K_2SO_4 + K_2MoO_4)$, $(Na_2CrO_4 + Na_2MoO_4)$, $(K_2CrO_4 + K_2MoO_4)$, and $(Na_2MoO_4 + K_2MoO_4)$.

Phase diagram data were very limited for Na₂MoO₄- and K₂MoO₄-containing commoncation ternary sub-systems, reciprocal ternary sub-systems (that is, systems with Na, K, and two anions), and higher order sub-systems. As will be discussed later, such data were only available for the (Na₂SO₄ + Na₂CrO₄ + Na₂MoO₄) and Na, K // Cl, MoO₄ sub-systems. The liquid solution exhibits small deviations from ideality. Hence, predictions in the entire multicomponent system (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂MoO₄ + Na₂Mo₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇ + K₂O) (diluted in free oxides) are expected to be reasonably accurate. All calculations and optimizations have been conducted using the FactSage thermochemical software. ¹⁸

2. Thermodynamic data, crystal structures and space groups for the pure compounds

Thermodynamic data $(\Delta H_{298.15 \text{ K}}^{\circ}, S_{298.15 \text{ K}}^{\circ}, \text{ and } C_P)$ for the condensed pure compounds of the $(NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7 + Na_2MoO_4 + Na_2Mo_2O_7 + Na_2O + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7 + K_2CrO_4 + K_2Cr_2O_7 + Na_2O_7 + K_2Cr_2O_7 + K_2Cr$

K₂MoO₄ + K₂Mo₂O₇ + K₂O) system were previously selected in references ^{4, 14, 17, 19, 20} and were directly used in the present study. The thermodynamic data for NaCl and KCl have been evaluated by Chartrand and Pelton. ¹⁹ Assessments of the thermodynamic properties of Na₂CO₃, Na₂SO₄, K₂CO₃, K₂SO₄, Na₂S₂O₇ and K₂S₂O₇ have been conducted by Lindberg et al. ^{14, 20} The thermodynamic data for Na₂CrO₄, K₂CrO₄, Na₂Cr₂O₇, K₂Cr₂O₇, Na₂MoO₄, K₂MoO₄, Na₂Mo₂O₇, and K₂Mo₂O₇ were taken directly from our previous works. ^{4, 17} Finally, the thermodynamic properties of Na₂O and K₂O were taken directly from the FToxid database in FactSage. ¹⁸ For every solid compound, the most probable crystal structure and space group were discussed previously based on the available information from the literature.

A summary of the crystal structures and space groups of all relevant pure salt compounds is displayed in Table 1. Note that new information taken from ^{4, 17} is presented only for Na₂MoO₄, Na₂Mo₂O₇, K₂MoO₄, and K₂Mo₂O₇. For all other solid compounds, the corresponding information was given previously, ¹⁶ and is repeated here for the sake of clarity.

The thermodynamic data for the condensed pure compounds optimized in the present study are given in Table 2.

Pure compound	Allotrope	Crystal structure	Space group	Pearson Symbol / Phase Prototype	Reference
NaCl	NaCl	Cubic	Fm3̄m (225)	cF8 / NaCl	FactSage (FTsalt
					database) ¹⁸

Table 1: Crystal structures and space groups of all relevant pure salt compounds

	1				
KCI	KCI	Cubic	Fm3m (225)	cF8 / NaCl	FactSage (FTsalt
Na ₂ CO ₃	$Na_2CO_3(S_1)$	Monoclinic	C2/m (12)	mS24 / γ-	database) ^{18, 21}
				Na ₂ CO ₃ -a	
	$Na_2CO_3(S_2)$	Monoclinic	C2/m (12)	mS24 / β-	
				Na ₂ CO ₃ -b	
	$Na_2CO_3(S_3)$	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	
K ₂ CO ₃	$K_2CO_3(S_1)$	Monoclinic	P2 ₁ /c (14)	mP24 / K ₂ CO ₃	FactSage (FTsalt
	$K_2CO_3(S_2)$	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	database) ¹⁸
Na ₂ SO ₄	Na ₂ SO ₄ (S ₃)	Orthorhombic	Fddd (70)	oF56 / Na ₂ SO ₄	FactSage (FTsalt
	$Na_2SO_4(S_1)$	Orthorhombic	Cmcm (63)	oS28 / Na ₂ CrO ₄	database) ¹⁸ , ¹⁴
	Na ₂ SO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	
Na ₂ S ₂ O ₇	Na ₂ S ₂ O ₇	Triclinic	P1 (2)	aP22 / Cd ₂ P ₂ O ₇	FactSage (FTsalt
					database) ¹⁸ , ^{22, 23}
K ₂ SO ₄	K ₂ SO ₄ (S ₁)	Orthorhombic	Pnma (62)	oP28 / K ₂ SO ₄	FactSage (FTsalt
	$K_2SO_4(S_2)$	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	database) ¹⁰ , ¹⁴
K ₂ S ₂ O ₇	K ₂ S ₂ O ₇ (S ₁)	Monoclinic	C2/c (15)	mS44 / K ₂ S ₂ O ₇	FactSage (FTsalt
	K ₂ S ₂ O ₇ (S ₂)	-	-	-	database) ¹⁰ , ²²
Na ₂ CrO ₄	Na ₂ CrO ₄ (S ₁)	Orthorhombic	Cmcm (63)	oS28 / Na ₂ CrO ₄	4, 24
	Na ₂ CrO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	*	
Na ₂ Cr ₂ O ₇	$Na_2Cr_2O_7(S_1)$	Triclinic	P1 (2)	aP44 /	17, 25, 26
				Na ₂ Cr ₂ O ₇	
	$Na_2Cr_2O_7(S_2)$	Triclinic	A1 (2)	aP22 / Cd ₂ P ₂ O ₇	
K ₂ CrO ₄	K ₂ CrO ₄ (S ₁)	Orthorhombic	Pnma (62)	oP28 / K ₂ SO ₄	4, 27
	K ₂ CrO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	*	
K ₂ Cr ₂ O ₇	$K_2Cr_2O_7(S_1)$	Triclinic	P1 (2)	aP44 / K ₂ Cr ₂ O ₇	17, 22, 28
	K ₂ Cr ₂ O ₇ (S ₂)	Monoclinic	P2 ₁ /c (14)	-	
Na ₂ MoO ₄	Na ₂ MoO ₄ (S ₁)	Cubic	Fd3m (227)	cF56 / MgAl ₂ O ₄	4, 22, 29
	Na2MoO4(S2)	Orthorhombic	Pbn2 ₁ (33)	-	
	Na ₂ MoO ₄ (S ₃)	Orthorhombic	Fddd (70)	**	
	Na2MoO4(S4)	Hexagonal	P6 ₃ /mmc (194)	*	
Na ₂ Mo ₂ O ₇	Na ₂ Mo ₂ O _{7(S1)}	Orthorhombic	Cmca D_{2h}^{18} (64)	oS88 / Na ₂ W ₂ O ₇	17, 30
	Na2Mo2O7(S2)	Monoclinic	-	-	
K2MoO4	K2MoO4(S1)	Monoclinic	C2/m (12)	mS28 / K ₂ MoO ₄	4, 22, 31
	K2MoO4(S2)	Orthorhombic	Cmcm (63)	***	

	K2MoO4(S3)	Trigonal	P3m1 (164)	-	
K2M02O7	K2M02O7(81)	Triclinic	P1 (2)	aP22 / K ₂ Mo ₂ O ₇	17, 22, 32
	K2M02O7(S2)	Monoclinic	$P2_1/c \text{ or } C_{2h}^5 -$	-	
		(assumption)	P2 ₁ /n		
			(assumption)		
			(14)		

* The corresponding Pearson symbols / prototypes for Na₂CrO₄(S₂), K₂CrO₄(S₂) and Na₂MoO₄(S₄) are not available to our knowledge. Thus, since these three compounds have the same crystal structure and space group as Na₂CO₃(S₃), Na₂SO₄(S₂), K₂CO₃(S₂), and K₂SO₄(S₂), they were assumed to have the same Pearson symbol / prototype phase (that is, hP22 / K₂SO₄).

** The corresponding Pearson symbol / prototype for Na₂MoO₄(S₃) is not available to our knowledge. Thus, since this compound has the same crystal structure and space group as Na₂SO₄(S₃), it was assumed to have the same Pearson symbol / prototype phase (that is, oF56 / Na₂SO₄).

^{***} The corresponding Pearson symbol / prototype for $K_2MoO_4(S_2)$ is not available to our knowledge. Thus, since this compound has the same crystal structure and space group as $Na_2CrO_4(S_1)$ and $Na_2SO_4(S_1)$, it was assumed to have the same Pearson symbol / prototype phase (that is, oS28 / Na₂CrO₄).

Compound	T Range (K)	$\Delta H_{298.15 \text{ K}}^{\circ}$ (J/mol) ^a	S°298.15 K (J/mol.K) ^b	C _P (J/mol.K)
Na ₃ ClMoO ₄	298.15 to 950	-1,872,914.8	248.5426	171.284592 + 0.09489312 <i>T</i> /K
K ₃ Na(MoO ₄) ₂ (below 513K)	298.15 to 564	-2,976,566.0	389.6457	232.914912 + 0.184602264 <i>T</i> /K + 1,094,534.4 (<i>T</i> /K) ⁻²

Table 2 : Thermodynamic properties of solid compounds optimized in the present study

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

^b Absolute (third law) entropy.

3. Thermodynamic model for the liquid phase

The liquid phase of the $(NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7 + Na_2MoO_4 + Na_2Mo_2O_7 + Na_2O + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7 + K_2CrO_4 + K_2Cr_2O_7 + K_2MoO_4 + K_2Mo_2O_7 + K_2O)$ system (diluted in free oxides) was modeled using the

Modified Quasichemical Model in the Quadruplet Approximation (MQMQA). ³³ The cations (Na⁺ and K⁺ in this work) and the anions (Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻, Mo₂O₇²⁻ and O²⁻ in this work) are distributed over a cationic and anionic sublattice, respectively. The MQMQA takes into account coupled 1st- and 2nd-nearest-neighbour short-range order (*i.e.* between sublattices and within a sublattice respectively). A quadruplet such as Na₂(MoO₄)₂, NaK(MoO₄)₂, Na₂(CO₃)(MoO₄) or NaK(CO₃)(MoO₄) consists of two 2nd-nearest-neighbour cations and two 2nd-nearest-neighbour anions, which are mutual 1st-nearest-neighbours. Quadruplets all have a Gibbs energy and are assumed to mix randomly, constrained by an elemental mass balance. The equilibrium quadruplet composition (configuration) is obtained by minimizing the Gibbs energy of the liquid solution at a given temperature, pressure and composition, and the equilibrium configuration reflects 1st- and 2nd-nearest-neighbour short-range order among ions.

The model is described in detail in reference ³³ and its main features were given in our previous work. ¹⁶ A brief summary is provided below.

Second-nearest-neighbour (cation-cation) short-range ordering is described in terms of the following equilibrium :

$$[A-X-A]_{pair} + [B-X-B]_{pair} = 2 [A-X-B]_{pair}; \quad \Delta g_{AB/X_2} \quad (1)$$

where A and B are two different cations (Na⁺ and K⁺ in this work), and X is an anion. The Gibbs energy change $\Delta g_{AB/X_2}$ is a model parameter that can be expressed as a function of composition by an empirical polynomial expression (see equation [11] in reference ³³). As $\Delta g_{AB/X_2}$ becomes progressively more negative, reaction (1) is shifted to the right, [A-X-B] pairs predominate and 2nd-nearest-neighbour (cation-cation) short-range ordering results. Random mixing occurs when $\Delta g_{AB/X_2}$ is zero. To a lesser extent, 2nd-nearest-neighbour anion-anion ordering can play a role. Hence, the following pair exchange reactions are also taken into account :

$$[X-A-X]_{pair} + [Y-A-Y]_{pair} = 2 [X-A-Y]_{pair}; \quad \Delta g_{A_2/XY} \quad (2)$$

where A is a cation (Na⁺ or K⁺ in this work), and X and Y are two different anions.

In the case of reciprocal salt solutions (that is, solutions with two or more cations, and two or more anions), first-nearest-neighbour (cation-anion) short-range ordering can occur. Its

extent is related to the Gibbs energy change for the following exchange reaction :

$$[A-X]_{pair} + [B-Y]_{pair} = [A-Y]_{pair} + [B-X]_{pair}; \quad \Delta g_{AB/XY}^{exchange} \quad (3)$$

where A and B are two different cations (Na⁺ and K⁺ in this work), and X and Y are two different anions. $\Delta g_{AB/XY}^{exchange}$ only depends on the Gibbs energies of the four pure liquid salts. If it is negative, then [A-Y] and [B-X] 1st-nearest-neighbour pairs predominate. For instance, $\Delta g_{NaK/Cl(MoO_4)}^{exchange}$ for the exchange reaction NaCl(1) + 0.5 K₂MoO₄(1) \leftrightarrow KCl(1) + 0.5 Na₂MoO₄(1) is calculated to be about -4.3 kJ/mol at 1250K (i.e. above the highest melting temperature of the four pure salts).

To obtain quantitative fits, small empirical "ternary reciprocal parameters" may have to be included in the liquid model. These parameters represent the Gibbs energies of formation of the ABXY quadruplets from the binary quadruplets ³³:

$$\frac{1}{2}(ABX_2 + ABY_2 + A_2XY + B_2XY) = 2(ABXY); \ \Delta g_{AB/XY} \ (4)$$

The model parameter $\Delta g_{AB/XY}$ is expanded as an empirical polynomial in the mole fractions x_{A_2/X_2} , x_{A_2/Y_2} , x_{B_2/X_2} and x_{B_2/Y_2} of the A₂X₂, A₂Y₂, B₂X₂ and B₂Y₂ unary quadruplets as follows:

$$\Delta g_{AB/XY} = \Delta g^{o}_{AB/XY} + \sum_{i \ge 1} \left[g^{i}_{AB/XY(AX)} x^{i}_{A_{2}/X_{2}} + g^{i}_{AB/XY(BX)} x^{i}_{B_{2}/X_{2}} + g^{i}_{AB/XY(AY)} x^{i}_{A_{2}/Y_{2}} + g^{i}_{AB/XY(BY)} x^{i}_{B_{2}/Y_{2}} \right]$$
(5)

The empirical parameters $\Delta g^{o}_{AB/XY}$ and $g^{i}_{AB/XY(AX)}$, etc. may be temperature-dependent and can be obtained by optimizing thermodynamic and phase diagram data in the ternary reciprocal system A, B // X, Y. They are all expected to be relatively small.

The 2nd-nearest-neighbour "coordination numbers" are model parameters, and are permitted to change with composition in the liquid solution. ³³ Such a flexibility permits to select the compositions of maximum short-range ordering in the A, B // X and A // X, Y common-ion binary systems through the ratios $(Z_{AB/X_2}^B/Z_{AB/X_2}^A)$ and $(Z_{A_2/XY}^Y/Z_{A_2/XY}^X)$, where Z_{AB/X_2}^i and $Z_{A_2/XY}^i$ are the 2nd-nearest-neighbour "coordination numbers" of the ion *i* when all *i* exist in ABX₂ and A₂XY quadruplets, respectively. "Default values" of the 2ndnearest-neighbour (cation-cation or anion-anion) "coordination numbers" for the ABXY quadruplets were proposed previously (equation [23] of reference ³³). These "default values" were used for the (Na₂SO₄ + K₂SO₄ + Na₂CrO₄ + K₂CrO₄), (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) and (Na₂CO₃ + K₂CO₃ + Na₂CrO₄ + K₂CrO₄) ternary reciprocal systems modeled in our previous work, ¹⁶ and for the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) ternary reciprocal system modeled in the present study.

It is required to designate all ternary common-cation sub-systems of the (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂MoO₄ + Na₂Mo₂O₇ + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇) main system as either "symmetric" or "asymmetric". ³⁴ The liquid model consists of the Na⁺ and K⁺ cations, and of the main anions Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻, Mo₂O₇²⁻. All anions are divided into two different chemical groups, based on their valence: group 1 = Cl⁻; and group $2 = CO_3^{2-}$, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻, Mo₂O₇²⁻.

For all ternary common-cation sub-systems containing NaCl or KCl, two anions belong to the same group and Cl⁻ belongs to another group; a Kohler-Toop-like (asymmetric) interpolation method is then used with Cl⁻ as the asymmetric component. For all ternary common-cation sub-systems without NaCl or KCl (such as $(Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4)$ modeled in the present work), all three anions belong to the same group; a Kohler-like (symmetric) interpolation method is then used.

Using the available experimental data (such as phase diagram data) for the A, B // X and A // X, Y common-ion binary systems, the model parameters $\Delta g_{AB/X_2}$ (reaction (1)) and $\Delta g_{A_2/XY}$ (reaction (2)) can be optimized through expansion as empirical polynomials in the composition variables χ_{ij} and χ_{ji} . After selecting an interpolation method for each ternary common-ion sub-system, χ_{ij} and χ_{ji} are defined unambiguously. ³⁴ For any ternary common-cation sub-system (AX + AY + AZ) (where A is Na⁺ or K⁺, and X, Y, Z are three different anions), terms may be included that give the effect of the third component, AZ, on the quadruplet-formation energy $\Delta g_{A_2/XY}$ of the binary A₂XY quadruplet. This is done by introducing the empirical ternary parameter $g_{A/XY(Z)}^{ijk}$, which can be obtained by optimizing thermodynamic and phase diagram data in the common-cation ternary system (AX + AY + AZ). ³⁴

The Gibbs energy of the solution can be expressed as follows:

$$G = \sum n_{ij/kl} g_{ij/kl} - T \Delta S^{\text{config}}$$
(6)

where $n_{ij/kl}$ refers to the number of moles of unary, binary, and reciprocal quadruplets; $g_{ij/kl}$ is the Gibbs energy of the quadruplets, and ΔS^{config} represents the configurational entropy of mixing. A random distribution of all quadruplets over "quadruplet positions" is assumed. However, no exact mathematical expression of ΔS^{config} is available for this distribution, and an approximate expression was thus proposed (equation [39] in reference ³³).

As explained in reference ³⁵, the MQMQA has been improved to address the limitation of the previous model when the Gibbs energy change $\Delta g_{AB/XY}^{exchange}$ of reaction (3) becomes very negative. The expression of the configurational entropy has been refined; slight modifications have been made in the interpolation expression of the Gibbs energy excess parameters in reciprocal systems; and the parameter ζ , related to the ratio between the 2nd-nearest-neighbour and 1st-nearest-neighbour "coordination numbers" for a species *i* (equation [17] in reference ³³), is no longer constant. In the improved version of the MQMQA, the notation $\zeta_{A/X}$ is used, and this parameter is defined as follows:

$$\zeta_{A/X} = 2Z^{A}_{A_2/X_2} Z^{X}_{A_2/X_2} / \left(Z^{A}_{A_2/X_2} + Z^{X}_{A_2/X_2} \right)$$
(7)

where Z_{A_2/X_2}^i is the 2nd-nearest-neighbour "coordination number" of the ion *i* (*i* = A, X) when all *i* exist in A₂X₂ quadruplets.

Tables 3 and 4 list, respectively, the values of the 2^{nd} -nearest-neighbour "coordination numbers" and of the newly optimized model parameters for the liquid phase of the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻, Mo₂O₇²⁻, O²⁻ reciprocal system (diluted in free oxides).

For the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻, Mo₂O₇²⁻, O²⁻ reciprocal system, the values of $\zeta_{A/X}$ (equation (7)) are:

$$\zeta_{A/X} = 4; \quad \zeta_{A/Cl} = 6 \tag{8}$$

where $A = Na^+$, K^+ ; and $X = CO_3^{2-}$, SO_4^{2-} , $S_2O_7^{2-}$, CrO_4^{2-} , $Cr_2O_7^{2-}$, MoO_4^{2-} , $Mo_2O_7^{2}$, O^{2-} .

Table 3: 2^{nd} -nearest-neighbour "coordination numbers" for the quadruplets ABXY of the newly optimized systems of the Na⁺, K⁺ // Cl⁻, CO_3^{2-} , SO_4^{2-} , $S_2O_7^{2-}$, CrO_4^{2-} ,

А	В	Х	Y	$Z^{\rm A}_{{\rm AB}/{ m XY}}$	$Z^{\rm B}_{{\rm AB}/{ m XY}}$	$Z_{AB/XY}^{X}$	$Z_{AB/XY}^{Y}$
Na	Na	Cl	Cl	6	6	6	6
Κ	Κ	Cl	Cl	6	6	6	6
Na	Na	CO_3	CO_3	3	3	6	6
Κ	Κ	CO_3	CO_3	3	3	6	6
Na	Na	SO_4	SO_4	3	3	6	6
Κ	Κ	SO_4	SO_4	3	3	6	6
Na	Na	S_2O_7	S_2O_7	3	3	6	6
Κ	Κ	S_2O_7	S_2O_7	3	3	6	6
Na	Na	CrO ₄	CrO_4	3	3	6	6
Κ	Κ	CrO ₄	CrO_4	3	3	6	6
Na	Na	Cr_2O_7	Cr_2O_7	3	3	6	6
Κ	Κ	Cr_2O_7	Cr_2O_7	3	3	6	6
Na	Na	MoO ₄	MoO ₄	3	3	6	6
Κ	Κ	MoO_4	MoO ₄	3	3	6	6
Na	Na	Mo_2O_7	Mo_2O_7	3	3	6	6
Κ	Κ	Mo_2O_7	Mo_2O_7	3	3	6	6
Na	Na	О	0	3	3	6	6
Κ	Κ	О	0	3	3	6	6
Na	Na	Cl	MoO_4	4	4	4	8
Κ	Κ	Cl	MoO ₄	4	4	4	8
Na	Na	CO_3	MoO_4	3	3	6	6
Na	Na	SO_4	MoO_4	3	3	6	6
Na	Na	CrO_4	MoO_4	3	3	6	6
Κ	K	CO_3	MoO_4	3	3	6	6
Κ	Κ	SO_4	MoO ₄	3	3	6	6
Κ	Κ	CrO_4	MoO_4	3	3	6	6
Na	Κ	MoO_4	MoO ₄	3	3	6	6
Κ	Κ	Cr_2O_7	Mo_2O_7	3	3	6	6
Na	Na	MoO ₄	Mo_2O_7	3	3	6	6
K	K	MoO ₄	Mo_2O_7	3	3	6	6

 $Cr_2O_7^{2-}, MoO_4^{2-}, Mo_2O_7^{2-}, O^{2-}$ liquid phase

The 2nd-nearest-neighbour "coordination numbers" for the ABXY quadruplets of the Na⁺, K⁺ // Cl⁻, CO_3^{2-} , SO_4^{2-} , $S_2O_7^{2-}$, CrO_4^{2-} , $Cr_2O_7^{2-}$, O^{2-} liquid phase were given previously by Lindberg et al. ^{14, 15} and in our previous work, ¹⁶ and they were directly used in the present work.

Table 4: Model parameters optimized in the present work for the Na⁺, K⁺ // Cl⁻, CO_3^{2-} , SO_4^{2-} , $S_2O_7^{2-}$, CrO_4^{2-} , $Cr_2O_7^{2-}$, MoO_4^{2-} , $Mo_2O_7^{2-}$, O^{2-} liquid phase (diluted in free oxides)

System	Model parameter (J/mol)
(NaCl + Na ₂ MoO ₄)	$\Delta g_{Na_2/(Cl)(MoO_4)} = 300.0\chi_{(Cl)(MoO_4)}$
$(KCl + K_2MoO_4)$	$\Delta g_{K_2/(Cl)(MoO_4)} = -1,100.0 + 500.0\chi_{(Cl)(MoO_4)} - 750.0\chi_{(MoO_4)(Cl)}$
(Na ₂ CO ₃ + Na ₂ MoO ₄)	$\Delta g_{Na_2/(CO_3)(MoO_4)} = 700.0$
$(\mathrm{K_2CO_3} + \mathrm{K_2MoO_4})$	$\Delta g_{K_2/(CO_3)(MoO_4)} = 1,050.0 + 650.0\chi_{(MoO_4)(CO_3)}$
$(Na_2SO_4 + Na_2MoO_4)$	$\Delta g_{\text{Na}_2/(\text{SO}_4)(\text{MoO}_4)} = -5,700.0 + 3,000.0\chi_{(\text{MoO}_4)(\text{SO}_4)}$
$(K_2SO_4 + K_2MoO_4)$	$\Delta g_{K_2/(SO_4)(MoO_4)} = 500.0 + 800.0\chi_{(SO_4)(MoO_4)}$
$(Na_2CrO_4 + Na_2MoO_4)$	$\Delta g_{Na_2/(CrO_4)(MoO_4)} = 1,000.0 - 1,200.0\chi_{(CrO_4)(MoO_4)} + 1,000.0\chi_{(MoO_4)(CrO_4)}$
$(K_2CrO_4 + K_2MoO_4)$	$\Delta g_{K_2/(CrO_4)(MoO_4)} = 2,000.0 + 1,500.0\chi_{(CrO_4)(MoO_4)}$
$(Na_2MoO_4 + K_2MoO_4)$	$\Delta g_{NaK/(MoO_4)_2} = -500.0 + 750.0 \chi_{NaK}$
$(Na_2MoO_4 + Na_2Mo_2O_7)$	$\Delta g_{\text{Na}_2/(\text{MoO}_4)(\text{Mo}_2\text{O}_7)} = -450.0\chi_{(\text{MoO}_4)(\text{Mo}_2\text{O}_7)} + 3,500.0\chi_{(\text{Mo}_2\text{O}_7)(\text{MoO}_4)}$
$(NaCl + Na_2MoO_4 + KCl + K_2MoO_4)$	$\Delta g_{NaK/(Cl)(MoO_4)} = 7,000.0x_{K_2/(MoO_4)_2}$

4. Thermodynamic model for the solid solutions

Several solid solutions were modeled in the Na⁺, K⁺ // Cl⁻, CO_3^{2-} , SO_4^{2-} , $S_2O_7^{2-}$, CrO_4^{2-} , $Cr_2O_7^{2-}$, MoO_4^{2-} , $Mo_2O_7^{2-}$ main system. Table 5 describes in detail all solid solutions considered in the present work, and lists all optimized model parameters. A large part of the information displayed in this table was given previously, ¹⁶ and is repeated here for the sake of clarity. The new work performed in this study refers to the addition in the relevant existing solid solutions of Na₂MoO₄, K₂MoO₄, Na₂Mo₂O₇, and / or K₂Mo₂O₇,

and to the introduction of new solid solutions ($K_2MoO_4(s_3)$ -ht-ss, cF56, and $Na_2MoO_4(s_2)$ -ss rich).

The Na⁺, K⁺// CO₃²⁻, SO₄²⁻, CrO₄²⁻, MoO₄²⁻ sub-system displays a hexagonal solid solution (hP22) at high temperatures with limited solubility of K₂MoO₄, and complete mutual miscibility over the entire composition range for the remaining salts. The MQMQA ³³ was used to model this reciprocal solid solution, with two sublattices (a cationic one and an anionic one). As explained previously, ¹⁶ the MQM is more suited than the Compound Energy Formalism (CEF) ³⁶⁻³⁸ to model complex solid solutions such as (Na₂SO₄ + K₂SO₄) dissolving divalent cation sulfates like CaSO₄, ZnSO₄ and PbSO₄. In particular, in a recent work, ³⁹ the MQM was used to add ZnSO₄ and PbSO₄ as solutes in the high-temperature (Na₂SO₄ + K₂SO₄) hexagonal solid solution. For the sake of consistency, the MQMQA was retained in the present work to model the hP22 solid solution (with Na⁺ and K⁺ as the cations, and CO₃²⁻, SO₄²⁻, CrO₄²⁻, and MoO₄²⁻ as the anions). All other solid solutions exhibited limited solubility, and were modeled with the CEF. ³⁶⁻³⁸ In most cases, two sublattices were required. However, three sublattices were used for the molybdenum-glaserite phase K₃Na(MoO₄)₂, which exhibits significant non-stoichiometry at temperatures above 240°C. ⁴⁰

As an example, let us consider the aP44 solid solution which consists of the triclinic lowtemperature allotropes Na₂Cr₂O_{7(S1)}, K₂Cr₂O_{7(S1)}, and K₂Mo₂O_{7(S1)} (mutually soluble) dissolving Na₂Mo₂O₇. The sublattice structure (Na⁺, K⁺)₂(Cr₂O₇²⁻, Mo₂O₇²⁻) was used, where Na⁺ and K⁺ reside on the cationic sublattice C while Cr₂O₇²⁻ and Mo₂O₇²⁻ reside on the anionic sublattice A. The molar Gibbs energy of the solution is given by the following expression :

$$\begin{split} G_{m} &= y_{Na}^{C} + y_{Cr_{2}O_{7}^{2}}^{A} - G_{Na^{+}:Cr_{2}O_{7}^{2}}^{\circ} + y_{K^{+}}^{C} y_{Cr_{2}O_{7}^{2}}^{A} - G_{K^{+}:Cr_{2}O_{7}^{2}}^{\circ} + y_{Na^{+}}^{C} y_{Mo_{2}O_{7}^{2}}^{A} - G_{Na^{+}:Mo_{2}O_{7}^{2}}^{\circ} \\ &+ y_{K}^{C} + y_{Mo_{2}O_{7}^{2}}^{A} - G_{K^{+}:Mo_{2}O_{7}^{2}}^{\circ} + 2RT \Big(y_{Na^{+}}^{C} \ln y_{Na^{+}}^{C} + y_{K^{+}}^{C} \ln y_{K^{+}}^{C} \Big) \\ &+ RT \Big(y_{Cr_{2}O_{7}^{2}}^{A} \ln y_{Cr_{2}O_{7}^{2}}^{A} + y_{Mo_{2}O_{7}^{2}}^{A} - \ln y_{Mo_{2}O_{7}^{2}}^{A} - \ln y_{Mo_{2}O_{7}^{2}}^{A} \Big) \\ &+ G^{E} \Big(9 \Big) \end{split}$$

The first four terms give the reference Gibbs energy of the solution, where $y_{Na^+}^C$ and $y_{K^+}^C$ are the site fractions of Na⁺ and K⁺ on the cationic sublattice C, and $y_{Cr_2O_7^{-}}^A$ and $y_{Mo_2O_7^{-}}^A$ are the site fractions of $Cr_2O_7^{2-}$ and $Mo_2O_7^{2-}$ on the anionic sublattice A. The standard molar Gibbs energies of the end-member components Na₂Cr₂O₇, K₂Cr₂O₇, Na₂Mo₂O₇ and K₂Mo₂O₇ are represented by $G^{\circ}_{Na^+:Cr_2O_7^{2-}}$, $G^{\circ}_{K^+:Cr_2O_7^{2-}}$, $G^{\circ}_{Na^+:Mo_2O_7^{2-}}$ and $G^{\circ}_{K^+:Mo_2O_7^{2-}}$, respectively.

Since the cations and anions are assumed to be randomly distributed on their respective sublattice, as in the Temkin-type, ⁴¹ the fifth and sixth terms in equation (9) correspond to the ideal entropy of mixing. The final term represents the molar excess Gibbs energy and is given by:

$$\begin{split} G^{E} &= y_{Na}^{C} + y_{K}^{C} + y_{Cr_{2}O_{7}^{2}}^{A} - L_{Na^{+},K^{+}:Cr_{2}O_{7}^{2}} + y_{Na}^{C} + y_{K}^{C} + y_{Mo_{2}O_{7}^{2}}^{A} - L_{Na^{+},K^{+}:Mo_{2}O_{7}^{2}} \\ &+ y_{Na}^{C} + y_{Cr_{2}O_{7}^{2}}^{A} - y_{Mo_{2}O_{7}^{2}}^{A} - L_{Na^{+}:Cr_{2}O_{7}^{2}} - Mo_{2}O_{7}^{2} - y_{K^{+}}^{C} + y_{Cr_{2}O_{7}^{2}}^{A} - y_{Mo_{2}O_{7}^{2}}^{A} - L_{K^{+}:Cr_{2}O_{7}^{2}} - Mo_{2}O_{7}^{2} - MO_{2}O_{7}^$$

In equation (10), the first four terms are interaction parameters in the four common-ion binary sub-systems, and the last term is a reciprocal interaction parameter. The L factors can be made temperature-dependent and also composition-dependent, where Redlich-Kister terms $L_{i>0}^{i}(y_{A} - y_{B})^{i}$ as a function of site fractions are generally employed.

Table 5: Description and list of optimized model parameters for the various solid solutions in the Na⁺, K⁺// Cl⁻, CO_3^{2-} , SO_4^{2-} , $S_2O_7^{2-}$, CrO_4^{2-} , $Cr_2O_7^{2-}$, MoO_4^{2-} , $Mo_2O_7^{2-}$ main system modeled in the present work

Hexagonal solid solution hP22

 $\label{eq:high-temperature allotropes Na_2CO_{3(S3)}, K_2CO_{3(S2)}, Na_2SO_{4(S2)}, K_2SO_{4(S2)}, Na_2CrO_{4(S2)}, K_2CrO_{4(S2)}, and Na_2MoO_{4(S4)} mutually soluble, and dissolving K_2MoO_4$

P6₃/mmc space group Sublattice structure: $(Na^+, K^+)_2(CO_3^{2-}, SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-})$ Use of the MQMQA

The Gibbs energies of the "end-members" are: $\mathring{g}_{Na_2CO_3} = \mathring{g}_{Na_2CO_{3(S3)}}$ $\mathring{g}_{K_2CO_3} = \mathring{g}_{K_2CO_{3(S2)}}$ $\mathring{g}_{Na_2SO_4} = \mathring{g}_{Na_2SO_{4(S2)}}$ $\mathring{g}_{K_2SO_4} = \mathring{g}_{K_2SO_{4(S2)}}$
$$\begin{split} g_{Na_{2}CrO_{4}}^{'} &= g_{Na_{2}CrO_{4(S2)}}^{'} \\ g_{K_{2}CrO_{4}}^{'} &= g_{K_{2}CrO_{4(S2)}}^{'} \\ g_{Na_{2}MoO_{4}}^{'} &= g_{Na_{2}MoO_{4(S4)}}^{'} \\ g_{K_{2}MoO_{4}}^{'} &= g_{K_{2}MoO_{4(S3)}}^{'} + 10 \text{ (J/mol)} \end{split}$$

The 2nd-nearest-neighbour coordination number of each cationic species is 3.0, and that of each anionic species is 6.0. Thus, all $\zeta_{A/X}$ are equal to 4.0 (with A = Na⁺, K⁺ and X = CO₃²⁻, SO₄²⁻, CrO₄²⁻ and MoO₄²⁻).

The following interaction parameters for $(Na_2CO_3 + Na_2SO_4)$, $(K_2CO_3 + K_2SO_4)$, $(Na_2CO_3 + K_2CO_3)$, $(Na_2SO_4 + K_2SO_4)$ and $Na_3 K // CO_3$, SO_4 were obtained previously: $\Delta g_{Na_2/(CO_3)(SO_4)} = 1,106.7 + 1,060.0 Y_{CO_3} (J/mol)^{20}$ (This is a Bragg-Williams type term and Y_{CO_3} is the equivalent site fraction of CO_3) $\Delta g_{K_2/(CO_3)(SO_4)} = 1,571.7 + 105.0 Y_{CO_3} (J/mol)^{20}$ $\Delta g_{NaK/(CO_3)_2} = 4,935.0 - 2,928.2Y_K (J/mol)^{20}$ $\Delta g_{NaK/(SO_4)_2} = 3,040.4 + (2,370.9 - 3.1241 \times T) Y_K (J/mol)^{14,20}$ $\Delta g_{NaK/(CO_3)(SO_4)} = 1,401.3 (J/mol)^{20}$

The following interaction parameters for $(Na_2CO_3 + Na_2CrO_4)$, $(K_2CO_3 + K_2CrO_4)$, $(Na_2SO_4 + Na_2CrO_4)$, $(K_2SO_4 + K_2CrO_4)$ and $(Na_2CrO_4 + K_2CrO_4)$ were obtained in our previous work ¹⁶:

 $\Delta g_{Na_2/(CO_3)(CrO_4)} = 8,000.0 - 1,800.0 Y_{CrO_4}$ (J/mol)

 $\Delta g_{K_2/(CO_3)(CrO_4)} = 5,600.0 - 800.0 Y_{CrO_4} (J/mol)$

 $\Delta g_{Na_2/(SO_4)(CrO_4)} = 800.0 (J/mol)$

 $\Delta g_{K_2/(SO_4)(CrO_4)} = 1,000.0 - 500.0 \text{ Y}_{SO_4}(\text{J/mol})$

 $\Delta g_{NaK/(CrO_4)_2} = 2,700.0 + (2,000.0 - 2.4500 \times T)Y_K (J/mol)$

The following MoO₄-based interaction parameters were obtained in the present work: $\Delta g_{Na_2/(CO_3)(MoO_4)} = 100,000.0 \text{ (J/mol)}$ $\Delta g_{K_2/(CO_3)(MoO_4)} = 100,000.0 \text{ (J/mol)}$ $\Delta g_{\text{Na}_2/(\text{SO}_4)(\text{MoO}_4)} = 500.0 - 5,000.0 \text{ Y}_{\text{SO}_4} - 1,600.0 \text{ Y}_{\text{MoO}_4} \text{ (J/mol)}$

 $\Delta g_{Na_2/(CrO_4)(MoO_4)} = 500.0 Y_{CrO_4} + 2,500.0 Y_{MoO_4}$ (J/mol)

 $\Delta g_{K_2/(SO_4)(MoO_4)} = 2,000.0 + 2,000.0 Y_{SO_4}$ (J/mol)

 $\Delta g_{K_2/(CrO_4)(MoO_4)} = 600.0 + 3,550.0 Y_{CrO_4} + 2,070.0 Y_{MoO_4} (J/mol)$

 $\Delta g_{NaK/(MoO_4)_2} = 3,500.0 \text{ (J/mol)}$

Solid solution K2MoO4(S3)-ht-ss

Trigonal high-temperature allotrope $K_2MoO_{4(S3)}$ dissolving $K_2SO_4,\,K_2CrO_4,\,Na_2MoO_4,\,Na_2SO_4$ and Na_2CrO_4

 $P\overline{3}m1$ space group Sublattice structure: $(K^+, Na^+)_2(MoO_4^{2-}, SO_4^{2-}, CrO_4^{2-})$

The Gibbs energies of the "end-members" are:

$$\begin{split} \hat{g}_{K_{2}MoO_{4}}^{'} &= \hat{g}_{K_{2}MoO_{4}(s3)}^{'} \\ \hat{g}_{K_{2}SO_{4}}^{'} &= \hat{g}_{K_{2}SO_{4}(s2)}^{'} + 6,129.6 \text{ (J/mol)} \\ \hat{g}_{K_{2}CrO_{4}}^{'} &= \hat{g}_{K_{2}CrO_{4}(s2)}^{'} + 7,363.8 \text{ (J/mol)} \\ \hat{g}_{Na_{2}MoO_{4}}^{'} &= \hat{g}_{Na_{2}MoO_{4}(s4)}^{'} + 10,250.8 \text{ (J/mol)} \\ \hat{g}_{Na_{2}SO_{4}}^{'} &= \hat{g}_{Na_{2}SO_{4}(s2)}^{'} + 6,129.6 \text{ (J/mol)} \\ \hat{g}_{Na_{2}CrO_{4}}^{'} &= \hat{g}_{Na_{2}CrO_{4}(s2)}^{'} + 7,322.0 \text{ (J/mol)} \end{split}$$

Solid solution oS28

 $\label{eq:constraint} \begin{array}{l} Orthorhombic \ low-temperature \ allotropes \ Na_2CrO_{4(S1)}, \ Na_2SO_{4(S1)} \ and \ K_2MoO_{4(S2)} \\ mutually \ soluble, \ and \ dissolving \ K_2CrO_4, \ Na_2CO_3, \ K_2SO_4, \ K_2CO_3 \ and \ Na_2MoO_4 \\ \end{array}$

Cmcm space group Sublattice structure: $(Na^+, K^+)_2(SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, CO_3^{2-})$

The Gibbs energies of the "end-members" are:

$$g_{Na_2CrO_4}^{\circ} = g_{Na_2CrO_{4(S1)}}^{\circ}$$

 $g_{Na_2SO_4}^{\circ} = g_{Na_2SO_{4(S1)}}^{\circ}$
 $g_{Na_2MoO_4}^{\circ} = g_{Na_2MoO_{4(S3)}}^{\circ} + 6,276.0 \text{ (J/mol)}$
 $g_{Na_2CO_3}^{\circ} = g_{Na_2CO_{3(S2)}}^{\circ} + 7,112.8 \text{ (J/mol)}^{20}$
 $g_{K_2CrO_4}^{\circ} = g_{K_2CrO_{4(S1)}}^{\circ} + (33,472.0 - 7.7404 \times T) \text{ (J/mol)}^{16}$
 $g_{K_2SO_4}^{\circ} = g_{K_2SO_{4(S1)}}^{\circ} + 33,472.0 \text{ (J/mol)}^{20}$
 $g_{K_2MoO_4}^{\circ} = g_{K_2MoO_{4}(S2)}^{\circ}$
 $g_{K_2CO_3}^{\circ} = g_{K_2CO_{3(S1)}}^{\circ} + 4,184.0 \text{ (J/mol)}^{20}$

The following Redlich-Kister interaction parameter for $(Na_2CO_3 + Na_2SO_4)$ was obtained previously:

 $L^{0}_{Na/(CO_{3})(SO_{4})} = 3,347.2 (J/mol)^{20}$

The following Redlich-Kister interaction parameters for $(Na_2CO_3 + Na_2CrO_4)$ and $(Na_2SO_4 + Na_2CrO_4)$ were obtained in our previous work ¹⁶:

 $L^{0}_{Na/(CrO_{4})(CO_{3})} = 100,000.0$ (J/mol)

 $L^{0}_{Na/(CrO_{4})(SO_{4})} = 3,000.0 \text{ (J/mol)}$

The following MoO₄-based Redlich-Kister interaction parameters were obtained in the present work:

$$\begin{split} L^0_{K/(CO_3)(MoO_4)} &= 100,000.0 ~(J/mol) \\ L^0_{Na/(SO_4)(MoO_4)} &= 100,000.0 ~(J/mol) \\ L^0_{Na/(CrO_4)(MoO_4)} &= 500.0 ~(J/mol) \\ L^0_{K/(SO_4)(MoO_4)} &= -26,000.0 ~(J/mol) \\ L^0_{K/(CrO_4)(MoO_4)} &= -19,500.0 ~(J/mol) \\ L^0_{NaK/(MoO_4)} &= 6,200.0 ~(J/mol) \end{split}$$

Solid solution oP28

Orthorhombic low-temperature allotropes K₂CrO_{4(S1)} and K₂SO_{4(S1)} mutually soluble, and dissolving Na₂CrO₄, K₂CO₃, Na₂SO₄, Na₂CO₃, K₂MoO₄ and Na₂MoO₄

Pnma space group Sublattice structure: $(K^+, Na^+)_2(SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, CO_3^{2-})$

The Gibbs energies of the "end-members" are:

$$\begin{split} g_{K_{2}CrO_{4}}^{\circ} &= g_{K_{2}CrO_{4}(S1)}^{\circ} \\ g_{K_{2}SO_{4}}^{\circ} &= g_{K_{2}SO_{4}(S1)}^{\circ} \\ g_{K_{2}CO_{3}}^{\circ} &= g_{K_{2}CO_{3}(S1)}^{\circ} + 209.2 \text{ (J/mol)}^{20} \\ g_{K_{2}MOO_{4}}^{\circ} &= g_{K_{2}MOO_{4}(S3)}^{\circ} + 13,388.8 \text{ (J/mol)} \\ g_{Na_{2}CrO_{4}}^{\circ} &= g_{Na_{2}CrO_{4}(S1)}^{\circ} + (13,388.8 + 2.7196 \times T) \text{ (J/mol)}^{16} \\ g_{Na_{2}SO_{4}}^{\circ} &= g_{Na_{2}SO_{4}(S1)}^{\circ} + (29,288.0 - 20.9200 \times T) \text{ (J/mol)}^{20} \\ g_{Na_{2}CO_{3}}^{\circ} &= g_{Na_{2}CO_{3}(S1)}^{\circ} + 20,920.0 \text{ (J/mol)}^{20} \\ g_{Na_{2}MoO_{4}}^{\circ(3)} &= g_{Na_{2}MoO_{4}(S1)}^{\circ} + 20,920.0 \text{ (J/mol)} \end{split}$$

The following Redlich-Kister interaction parameters for (K₂CO₃ + K₂SO₄) were obtained

previously: $L^{0}_{K/(CO_{3})(SO_{4})} = 3,765.6 \text{ (J/mol)}^{20}$ $L^{1}_{K/(CO_{3})(SO_{4})} = -2,008.3 \text{ (J/mol)}^{20}$

The following Redlich-Kister interaction parameters for $(K_2CO_3 + K_2CrO_4)$ and (K_2SO_4)

+ K₂CrO₄) were obtained in our previous work ¹⁶:

 $L^{0}_{K/(CO_{3})(CrO_{4})} = 17,500.0 (J/mol)$

 $L^{1}_{K/(CO_{3})(CrO_{4})} = 3,000.0 \text{ (J/mol)}$

 $L^{0}_{K/(CrO_{4})(SO_{4})} = 1,800.0 \text{ (J/mol)}$

Glaserite solid solution hP14

Solid K₃Na(SO₄)₂, K₃Na(CrO₄)₂ and K₃Na(MoO₄)₂ mutually soluble, and dissolving Na⁺

 $P\overline{3}m1$ space group

Sublattice structure: $(K^+, Na^+)_3 (Na^+) (SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-})_2$

The Gibbs energies of the "end-members" are: $g_{K_3Na(SO_4)_2}^{\circ} = 1.5 \times g_{K_2SO_4(S1)}^{\circ} + 0.5 \times g_{Na_2SO_4(S2)}^{\circ} - 10,878.4 + 9.7906 \times T \text{ (J/mol)}$ $g_{Na_3Na(SO_4)_2}^{\circ} = 2 \times g_{Na_2SO_4(S2)}^{\circ} + 16,736.0 - 10.7110 \times T \text{ (J/mol)}^{14}$ $g_{K_3Na(CrO_4)_2}^{\circ} = 1.5 \times g_{K_2CrO_4(S1)}^{\circ} + 0.5 \times g_{Na_2CrO_4(S1)}^{\circ} - 17,154.4 + 9.4140 \times T \text{ (J/mol)}^{16}$ $g_{Na_3Na(CrO_4)_2}^{\circ} = 2 \times g_{Na_2CrO_4(S1)}^{\circ} + 12,970.4 - 8.1588 \times T \text{ (J/mol)}^{16}$ $g_{K_3Na(MoO_4)_2}^{\circ} = 1.5 \times g_{K_2MoO_4(S3)}^{\circ} + 0.5 \times g_{Na_2MoO_4(S4)}^{\circ} - 10,460.0 \text{ (J/mol)}$ $g_{Na_3Na(MoO_4)_2}^{\circ} = 2 \times g_{Na_2MoO_4(S4)}^{\circ} + 23,012.0 \text{ (J/mol)}$

Solid solution oF56

 $Orthorhombic \ low-temperature \ allotropes \ Na_2SO_{4(S3)} \ and \ Na_2MoO_{4(S3)} \ mutually \ soluble, and \ dissolving \ Na_2CrO_4, \ K_2SO_4, \ K_2CrO_4 \ and \ K_2MoO_4$

Fddd space group Sublattice structure: $(Na^+, K^+)_2(SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-})$

The Gibbs energies of the "end-members" are: $\mathring{g}_{Na_2SO_4} = \mathring{g}_{Na_2SO_{4(S3)}}$
$$\begin{split} \hat{g}_{K_{2}SO_{4}}^{\circ} &= \hat{g}_{K_{2}SO_{4}(S1)}^{\circ} + 66,944.0 \text{ (J/mol)}^{16} \\ \hat{g}_{Na_{2}CrO_{4}}^{\circ} &= \hat{g}_{Na_{2}CrO_{4}(S1)}^{\circ} + 4,100.3 \text{ (J/mol)}^{16} \\ \hat{g}_{K_{2}CrO_{4}}^{\circ} &= \hat{g}_{K_{2}CrO_{4}(S1)}^{\circ} + 66,944.0 \text{ (J/mol)}^{16} \\ \hat{g}_{Na_{2}MoO_{4}}^{\circ} &= \hat{g}_{Na_{2}MoO_{4}(S3)}^{\circ} \\ \hat{g}_{K_{2}MoO_{4}}^{\circ} &= \hat{g}_{K_{2}MoO_{4}(S3)}^{\circ} + (-7,531.2 + 37.0284 \times T) \text{ (J/mol)} \end{split}$$

The following MoO₄-based Redlich-Kister interaction parameters were obtained in the present work:

 $L^0_{NaK/MoO_4} = -18,000.0 (J/mol)$

 $L_{NaK/MoO_4}^1 = 15,000.0 (J/mol)$

 $L^{0}_{Na/(SO_{4})(MoO_{4})} = 100,000.0 \text{ (J/mol)}$

 $L^{0}_{Na/(CrO_{4})(MoO_{4})} = 100,000.0 \text{ (J/mol)}$

Solid solution cF56

Cubic low-temperature allotrope Na2MoO4(S1) dissolving Na2SO4 and Na2CrO4

 $Fd\overline{3}m$ space group Sublattice structure: $(Na^+)_2(MoO_4^{2-}, SO_4^{2-}, CrO_4^{2-})$

The Gibbs energies of the "end-members" are:

$$\begin{split} \hat{g_{Na_2MoO_4}} &= \hat{g_{Na_2MoO_{4(S1)}}} \\ \hat{g_{Na_2SO_4}} &= \hat{g_{Na_2SO_{4(S1)}}} + (8,368.0 + 16.7360 \times T) \text{ (J/mol)} \\ \hat{g_{Na_2CrO_4}} &= \hat{g_{Na_2CrO_{4(S1)}}} + (8,368.0 + 16.7360 \times T) \text{ (J/mol)} \end{split}$$

Solid solution Na₂MoO_{4(S2)}-ss-rich

Orthorhombic intermediate-temperature allotrope $Na_2MoO_{4(S2)}$ dissolving Na_2SO_4 and Na_2CrO_4

Pbn2₁ space group Sublattice structure: $(Na^+)_2(MoO_4^{2-}, SO_4^{2-}, CrO_4^{2-})$

The Gibbs energies of the "end-members" are:

$$\begin{split} \hat{g_{Na_2MoO_4}} &= \hat{g_{Na_2MoO_{4(S2)}}} \\ \hat{g_{Na_2SO_4}} &= \hat{g_{Na_2SO_{4(S2)}}} + (1,046.0 + 16.7360 \times T) \text{ (J/mol)} \\ \hat{g_{Na_2CrO_4}} &= \hat{g_{Na_2CrO_{4(S2)}}} + (1,046.0 + 16.7360 \times T) \text{ (J/mol)} \end{split}$$

Solid solution aP22

Triclinic allotropes $Na_2S_2O_7$ and $Na_2Cr_2O_{7(S2)}$ mutually soluble, and dissolving $K_2S_2O_7$ and $K_2Cr_2O_7$

 $A\overline{1}$ space group

Sublattice structure: $(Na^+, K^+)_2(S_2O_7^{2-}, Cr_2O_7^{2-})$

The Gibbs energies of the "end-members" are:

$$\begin{split} & \mathring{g_{Na_2S_2O_7}} = \mathring{g_{Na_2S_2O_7(S)}} \\ & \mathring{g_{K_2S_2O_7}} = \mathring{g_{K_2S_2O_7(S2)}} + 29,288.0 \text{ (J/mol)}^{14} \\ & \mathring{g_{Na_2Cr_2O_7}} = \mathring{g_{Na_2Cr_2O_7(S2)}} \\ & \mathring{g_{K_2Cr_2O_7}} = \mathring{g_{K_2Cr_2O_7(S2)}} + 7,531.2 + 5.6484 \times T \text{ (J/mol)}^{16} \end{split}$$

Solid solution aP44

 $\label{eq:constraint} \begin{array}{l} \mbox{Triclinic low-temperature allotropes $Na_2Cr_2O_{7(S1)}$, $K_2Cr_2O_{7(S1)}$ and $K_2Mo_2O_{7(S1)}$ mutually soluble, and dissolving $Na_2Mo_2O_7$ \\ \end{array}$

 $P\overline{1}$ space group

Sublattice structure: $(K^+, Na^+)_2(Cr_2O_7^{2-}, Mo_2O_7^{2-})$

The Gibbs energies of the "end-members" are:

$$\begin{split} \ddot{g}_{Na_{2}Cr_{2}O_{7}}^{n} &= \ddot{g}_{Na_{2}Cr_{2}O_{7}(S1)}^{n} \\ \ddot{g}_{K_{2}Cr_{2}O_{7}}^{n} &= \ddot{g}_{K_{2}Cr_{2}O_{7}(S1)}^{n} \\ \ddot{g}_{K_{2}MO_{2}O_{7}}^{n} &= \ddot{g}_{K_{2}MO_{2}O_{7}(S1)}^{n} \\ \dot{g}_{Na_{2}MO_{2}O_{7}}^{n} &= \ddot{g}_{Na_{2}MO_{2}O_{7}(S1)}^{n} + 11,296.8 + 3.8911 \times T \text{ (J/mol)} \end{split}$$

The following Redlich-Kister interaction parameter for $(Na_2Cr_2O_7 + K_2Cr_2O_7)$ was

obtained in our previous study ¹⁶ :

 $L_{NaK/Cr_2O_7}^0 = 20,000.0 \text{ (J/mol)}$

The following Mo₂O₇-based Redlich-Kister interaction parameter was obtained in the present work:

 $L^{0}_{K/(Cr_{2}O_{7})(Mo_{2}O_{7})} = 2,000.0 \text{ (J/mol)}$

Solid solution K₂Cr₂O₇(s.s)

Monoclinic high-temperature allotropes $K_2Cr_2O_{7(S2)}$ and $K_2Mo_2O_{7(S2)}$ mutually soluble, and dissolving $Na_2Cr_2O_7$ and $Na_2Mo_2O_7$

 $P2_1/c$ space group

Sublattice structure: $(K^+, Na^+)_2(Cr_2O_7^{2-}, Mo_2O_7^{2-})$

The Gibbs energies of the "end-members" are: $\overset{\circ}{g}_{K_{2}Cr_{2}O_{7}}^{e} = \overset{\circ}{g}_{K_{2}Cr_{2}O_{7}(S_{2})}^{e}$ $\overset{\circ}{g}_{Na_{2}Cr_{2}O_{7}}^{e} = \overset{\circ}{g}_{Na_{2}Cr_{2}O_{7}(S_{2})}^{e} + 11,296.8 + 3.8911 \times T (J/mol)^{16}$ $\overset{\circ}{g}_{K_{2}MO_{2}O_{7}}^{e} = \overset{\circ}{g}_{K_{2}MO_{2}O_{7}(S_{2})}^{e}$ $\overset{\circ}{g}_{Na_{2}MO_{2}O_{7}}^{(5)} = \overset{\circ}{g}_{Na_{2}MO_{2}O_{7}(S_{2})}^{e} + 11,296.8 + 3.8911 \times T (J/mol)$

The following Mo₂O₇-based Redlich-Kister interaction parameter was obtained in the

present work:

 $L^{0}_{K/(Cr_{2}O_{7})(Mo_{2}O_{7})} = 2,000.0 \text{ (J/mol)}$

Rocksalt solid solution cF8

Cubic NaCl and KCl mutually soluble

Fm3m space group

The Gibbs energies of the "end-members" are: $\mathring{g}_{NaCl} = \mathring{g}_{NaCl(S)}$ $\mathring{g}_{KCl} = \mathring{g}_{KCl(S)}$

The following Redlich-Kister interaction parameters for (NaCl + KCl) were obtained previously:

$$L_{NaK/Cl}^{0} = 15,972.0 + 32.7960 \times T - 5.593 \times T \times ln(T) (J/mol)^{42}$$

 $L_{NaK/Cl}^{1} = 1,639.0 (J/mol)^{42}$

^{(1),(2)} The "end-members" Na₂SO₄ and Na₂CrO₄ were added to the K₂MoO_{4(S3)}-ht-ss solid solution. The corresponding Gibbs energies are those of Na₂SO_{4(S2)} and Na₂CrO_{4(S2)} augmented by a positive Gibbs energy, respectively. The latter were assumed to be identical to those for the "end-members" K₂SO₄ (i.e. 6,129.6 J/mol) and K₂CrO₄ (i.e. 7,322.0 J/mol), respectively. The "end-members" Na₂SO₄ and Na₂CrO₄ are only required for calculations in the K, Na // MoO₄, SO₄ and K, Na // MoO₄, CrO₄ reciprocal systems, respectively, and higher-order systems.

⁽³⁾ The "end-member" Na₂MoO₄ was added to the oP28 solid solution. The corresponding Gibbs energy is that of Na₂MoO_{4(S1)} augmented by a positive Gibbs energy. As a first approximation, the latter was assumed to be identical to that for the "end-member" Na₂CO₃ (i.e. 20,920.0 J/mol). The "end-member" Na₂MoO₄ is only required for calculations in the K, Na // SO₄, MoO₄ and K, Na // CrO₄, MoO₄ reciprocal systems, and higher-order systems.

^{(4),(5)} The "end-member" Na₂Mo₂O₇ was added to both of the solid solutions aP44 and K₂Cr₂O₇(s.s). The corresponding Gibbs energies are those of Na₂Mo₂O_{7(S1)} and Na₂Mo₂O_{7(S2)} augmented by a positive Gibbs energy, respectively. As a first approximation, the latter were assumed to be identical to that for the "end-member" Na₂Cr₂O₇ in the K₂Cr₂O₇(s.s) solid solution (that is, 11,296.8 + 3.8911 × *T* J/mol), which was obtained in our previous work. The "end-member" Na₂Mo₂O₇ is only required for calculations in the K, Na // Cr₂O₇, Mo₂O₇ ternary reciprocal system and higher-order systems.

5. Experimental procedure

5.1 DSC-TGA

Materials and measurements

The present work was carried out using high purity gases (99.999% pure Ar, 99.999% pure N₂, and 99.999% pure CO₂) from Oy Linde Gas AB (Finland). For all initial solid reagents (Na₂CO₃, Na₂SO₄, K₂SO₄, Na₂CrO₄.4H₂O, K₂CrO₄, Na₂MoO₄, and K₂MoO₄), the supplier's name, CAS number and purity are reported in Table 6.

Chemical formula	Supplier	CAS number	Purity (%)
Na ₂ CO ₃	Sigma-Aldrich	<u>497-19-8</u>	≥ 99.95
Na ₂ SO ₄	Sigma-Aldrich	<u>7757-82-6</u>	≥ 99.0
K ₂ SO ₄	Sigma-Aldrich	<u>7778-80-5</u>	≥ 99.0
Na ₂ CrO ₄ .4H ₂ O	Sigma-Aldrich	<u>10034-82-9</u>	99.0
K ₂ CrO ₄	Alfa-Aesar	<u>7789-00-6</u>	99.9
Na ₂ MoO ₄	Sigma-Aldrich	<u>7631-95-0</u>	99.9
K ₂ MoO ₄	Sigma-Aldrich	<u>13446-49-6</u>	98

Table 6 : Purity and origin of the solid reagents used in our experiments

The binary common-ion sub-systems (Na₂CO₃ + Na₂MoO₄), (K₂SO₄ + K₂MoO₄), (Na₂CrO₄ + Na₂MoO₄), (K₂CrO₄ + K₂MoO₄) and (Na₂MoO₄ + K₂MoO₄) were investigated by DSC-TGA using a NETZSCH STA 449 F1 Jupiter® instrument at compositions where experimental phase diagram data were lacking in the literature. Additional DSC-TGA

measurements were carried out using the SDT Q600 TA Instrument (New Castle, DE, U.S.A.). Such measurements were made in the binary common-ion sub-systems (Na₂SO₄ + Na₂MoO₄) and (K₂SO₄ + K₂MoO₄). The SDT Q600 TA Instrument can perform baseline-free runs. Thus, the baseline is not horizontal as shown, for instance, in the thermogram displayed in Figure 6.

A detailed description of the calibration of the NETZSCH STA 449 F1 Jupiter® instrument was given in our previous work. ⁴ The experimental error for the temperatures was estimated as $\pm 1^{\circ}$ C. The SDT Q600 TA Instrument was calibrated by measuring the temperatures of fusion of high purity zinc, aluminum and gold. The experimental error for the temperatures was estimated as $\pm 2^{\circ}$ C. The mass change and heat flux upon heating and cooling were measured simultaneously.

All pure compounds used in the present study were dehydrated prior to the DSC-TGA measurements. Further information can be found in reference ⁴. Pt/Rh (80/20) and Al₂O₃ (corundum) crucibles were employed for the DSC-TGA measurements, using the NETZSCH STA 449 F1 Jupiter® instrument and the SDT Q600 TA Instrument, respectively.

All DSC-TGA measurements performed in the present work are reported in the Supporting Information (see Tables S1 to S9).

Flow rates of 90 ml/min CO₂ and 10 ml/min Ar were used as the shielding gas for all runs related to the three (Na₂CO₃ + Na₂MoO₄) binary mixtures investigated. A saturated CO₂ atmosphere was maintained to prevent dissociation of Na₂CO₃ at high temperatures into Na₂O_(s) and CO_{2(g)} and/or partial volatilization. Five other compositions were studied under CO₂-free conditions, including the composition of (78.0 mol% Na₂CO₃ + 22.0 mol% Na₂MoO₄) previously measured in the presence of CO₂(g).

A flow rate of 70 ml/min Ar was used as the shielding gas for all runs performed in the $(K_2SO_4 + K_2MoO_4)$, $(Na_2CrO_4 + Na_2MoO_4)$, $(K_2CrO_4 + K_2MoO_4)$ and $(Na_2MoO_4 + K_2MoO_4)$ binary sub-systems. Finally, the $(Na_2SO_4 + Na_2MoO_4)$ and $(K_2SO_4 + K_2MoO_4)$ binary sub-systems were investigated using a flow rate of 70 ml/min N₂.

For all DSC-TGA experiments conducted in the present work, an approach similar to that used in our previous study was adopted. ⁴ That is, the sample and reference were initially

heated from room temperature to 40°C, and then kept at constant temperature for 10 minutes to ensure thermal stability. Then, three consecutive heating-cooling cycles were conducted for each sample, with a heating/cooling rate of 10°C/min.

Mass loss was measured continuously throughout the experiments, with a maximum mass loss target of 3%.

Usually, only heating runs were taken into account. Each solid-solid transition was defined as the temperature at the onset of the peak while each liquidus temperature and eutectic temperature was defined as the temperature at the maximum of the peak. ⁴³

To avoid including non-reproducible data resulting from the thermal history of the sample, the first heating/cooling cycle was usually excluded from our analysis. However, for the two equilibrated molybdenum-glaserite compositions investigated in this work (see Table S9 in the Supporting Information), the first heating/cooling cycle was also considered since the corresponding samples had been equilibrated for four weeks at 400°C prior to the DSC-TGA measurements.

To perform the equilibration process of the molybdenum-glaserite phase, pre-treated pure powders of Na₂MoO₄ and K₂MoO₄ were mechanically mixed at the stoichiometric composition of (35 mol% Na₂MoO₄ + 65 mol% K₂MoO₄). This mixture was sealed in a fused silica tube, heated from room temperature to 800°C for 50 minutes at a heating rate of 15°C/min, and then cooled to 400°C at a cooling rate of 15°C/min for 27 minutes in a muffle furnace. After annealing at 400°C for four weeks under a flow rate of approximately 1 ml/min Ar, the equilibrated sample was quenched in air, mechanically ground, and analyzed subsequently by scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDS) and DSC-TGA.

5.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

The equilibrated molybdenum-glaserite (solid solution of 35 mol% $Na_2MoO_4 + 65$ mol% K_2MoO_4) after quenching was analyzed at room temperature with a LEO 1450 scanning electron microscope (SEM) (Carl Zeiss Microscopy GmbH, Jena, Germany) coupled with

an Oxford Instruments X-Max 50 mm² energy dispersive spectrometer (EDS) (Oxford Instruments plc, Abingdon, Oxfordshire, UK).

To confirm the formation of the molybdenum-glaserite phase, EDS analyses were conducted on six different crystals. The analytical results for those selected crystals are presented in Table 7, with a corresponding experimental error of $\pm 5\%$. For three crystals, the estimated compositions of the equilibrated sample were in good agreement with the composition of the original mechanical mixture, whereas there were some discrepancies for the other three crystals. Overall, our results confirmed the global homogeneity of the equilibrated molybdenum-glaserite phase. The estimated composition of this phase is $K_{1.29}Na_{0.70}Mo_{0.98}O_{3.92}$ while the original mechanical mixture had the composition $K_{1.3}Na_{0.7}MoO_4$.

SEM image spots for which the EDS analyses were conducted are presented in Figure S1 of the Supporting Information.

Element	Spectrum 3	Spectrum 5	Spectrum 7	Average
0	4.275	3.644	3.841	3.920
Na	0.700	0.700	0.700	0.700
K	1.272	1.234	1.364	1.291
Мо	0.954	0.945	1.032	0.977
K / (Na + K)	0.645	0.638	0.661	0.648
(Na + K) / Mo	2.066	2.050	1.999	2.037

Table 7: EDS analysis results of selected spectra for the quenched molybdenum-glaserite sample with an estimated experimental error of ±5%

6. Molybdate-based common-ion binary sub-systems

This section describes all MoO₄-based and Mo₂O₇-based common-ion binary sub-systems

for which thermodynamic data (mainly phase equilibria) were available. Calculation of the phase diagrams was made in air ($p(O_2) = 0.21$ atm). The gas phase was assumed to be ideal, and all gaseous species were taken from the FactPS database in FactSage ¹⁸. These were C, C₂, C₃, C₄, C₅, O, O₂, O₃, CO, C₂O, CO₂, C₃O₂, Na, Na₂, NaO, S, S₂, S₃, S₄, S₅, S₆, S₇, S₈, CS, CS₂, SO, SO₂, SO₃, SSO, COS, Na₂SO₄, Cl, Cl₂, CCl, C₂Cl, CCl₂, C₂Cl₂, CCl₃, C₂Cl₃, CCl₄, C₂Cl₄, C₂Cl₅, C₂Cl₆, C₆Cl₆, ClO, ClO₂, ClO₃, Cl₂O, ClOOCl, ClOClO, ClClOO, COCl, COCl₂, NaCl, (NaCl)₂, SCl, S₂Cl, SCl₂, ClSSCl, SOCl₂, SO₂Cl₂, K, K₂, KO, K₂SO₄, KCl, (KCl)₂, Cr, CrO, CrO₂, CrO₃, CrS, CrCl, CrCl₂, CrCl₃, CrCl₄, CrCl₅, CrCl₆, CrOCl, CrO₂Cl, CrOCl₂, CrO₂Cl₂, CrOCl₃, CrOCl₄, Mo, Mo₂, MoO, MoO₂, MoO₃, Mo₂O₆, Mo₃O₉, Mo₄O₁₂, Mo₅O₁₅, Mo(CO)₆, MoCl₄, MoCl₅, MoCl₆, and MoO₂Cl₂.

The possible reactions 2 $A_2MO_4 = A_2M_2O_7 + A_2O$ (where A = Na, K and M = Mo, Cr) were taken into account in the calculated phase diagrams for all MO₄-based binary subsystems. However, those reactions were shown to be very limited up to temperatures above the liquidus. ¹⁷

6.1 The (NaCl + Na₂MoO₄) system

The phase diagram has been measured by Bukhalova and Mateiko⁴⁴ using the visualpolythermal method. These authors reported the existence of the intermediate compound NaCl.Na₂MoO₄ melting congruently at around 644°C, with the presence of a flat maximum. Bukhalova and Mateiko⁴⁴ reported two eutectics at 40.8 mol% Na₂MoO₄ and 628°C, and at 68.1 mol% Na₂MoO₄ and 606°C. The calculated characteristics of these eutectics are 42.6 mol% Na₂MoO₄ and 642°C, and 77.6 mol% Na₂MoO₄ and 612°C, respectively. The experimental characteristics of the two eutectics have limited accuracy owing to the experimental technique that was used.

The compound Na₃ClMoO₄ was considered in the present work. Its Gibbs energy was estimated by starting with a Gibbs energy of formation from the pure end members [NaCl_(S) + Na₂MoO_{4(S1)} = Na₃ClMoO_{4(S)}] equal to zero. Then, $\Delta H^{\circ}_{298.15 \text{ K}}$ and $S^{\circ}_{298.15 \text{ K}}$ were adjusted to best reproduce the measured eutectic temperatures and temperature of fusion, ⁴⁴ while ensuring that the compound was calculated to remain stable at room temperature. The optimized thermodynamic properties ($\Delta H^{\circ}_{298.15 \text{ K}}$, $S^{\circ}_{298.15 \text{ K}}$, and C_P) of solid Na₃ClMoO₄ are given in Table 2; they correspond to an enthalpy of formation of 4,075.1 J/mol and an entropy of formation of 17.0000 J/mol-K. The calculated (NaCl + Na₂MoO₄) phase diagram in air ($p(O_2) = 0.21$ atm) is shown along with the measurements in Figure 1.



Figure 1: Calculated (NaCl + Na2MoO4) phase diagram in air (p(O2) = 0.21 atm). Experimental data from Bukhalova and Mateiko ⁴⁴ (●)

6.2 The (KCl + K_2MoO_4) system

The phase diagram has been measured using the visual-polythermal method. ⁴⁴ According to Bukhalova and Mateiko, ⁴⁴ (KCl + K₂MoO₄) is a simple eutectic system with no reported solid solutions or intermediate compounds. These authors reported a eutectic at 36.9 mol% K₂MoO₄ and 622°C. The calculated characteristics of the eutectic are 36.0 mol% K₂MoO₄ and 624°C.

The calculated (KCl + K_2MoO_4) phase diagram in air (p(O₂) = 0.21 atm) is compared to the measurements in Figure 2.



Figure 2: Calculated (KCl + K₂MoO₄) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Bukhalova and Mateiko ⁴⁴ (●)

6.3 The $(Na_2CO_3 + Na_2MoO_4)$ system

The phase diagram has been measured by Shurdumov et al. ⁴⁵ using thermal analysis. A eutectic was reported by these authors at 67.0 mol% Na₂MoO₄ and 588°C. The calculated characteristics of the eutectic are 66.8 mol% Na₂MoO₄ and 586°C. No solid solutions or intermediate compounds were reported. The measured limiting slopes of the Na₂CO₃ and Na₂MoO₄ liquidus curves at $x(Na_2CO_3) = 1$ and $x(Na_2MoO_4) = 1$ respect the limiting liquidus slope equation (11), which assumes no solid solubility :

$$\left(\frac{\mathrm{d}T}{\mathrm{d}x_{\mathrm{m}}^{\mathrm{liquidus}}}\right) = \frac{\mathrm{R}T_{\mathrm{fusion}(\mathrm{m})}^{2}}{\Delta h_{\mathrm{fusion}(\mathrm{m})}^{2}} \text{ at } [x_{m} = 1]$$
(11)

where $\Delta h_{\text{fusion(m)}}^{\circ}$ and $T_{\text{fusion(m)}}$ are, respectively, the enthalpy and temperature of fusion of the pure salt m. The high-temperature allotropes Na₂CO_{3(S3)} and Na₂MoO_{4(S4)} have the same hexagonal crystal structure and space group P6₃/mmc (see Table 1). A constant interaction parameter of +100,000.0 J/mol was introduced in the hP22 solid solution in order to calculate negligible mutual solid solubility.

In the present work, DSC-TGA measurements were performed for several binary mixtures with various contents of Na₂MoO₄, in the absence or presence of $CO_2(g)$: 2.5, 12.7, 22, 90 and 95 mol% (from 300 to 860°C, and in the absence of $CO_2(g)$); 22 mol% (from 300 to 830°C, and in the presence of $CO_2(g)$); and 50 and 85 mol% (from 300 to 700°C, and in the presence of $CO_2(g)$). As an example, the DSC thermogram for the binary composition (78 mol% Na₂CO₃ + 22 mol% Na₂MoO₄) in the presence of $CO_2(g)$ is displayed in Figure 3.

The calculated ($Na_2CO_3 + Na_2MoO_4$) phase diagram in air ($p(O_2) = 0.21$ atm) is shown along with the experimental data in Figure 4. As seen in this figure, our experimental thermal arrests agree satisfactorily with the solid-solid transitions $Na_2MoO_{4(S1)} =$ $Na_2MoO_{4(S2)}$ ⁴, $Na_2CO_{3(S2)} = Na_2CO_{3(S3)}$ ²⁰ and $Na_2MoO_{4(S3)} = Na_2MoO_{4(S4)}$.⁴ Our measured liquidus temperatures in the presence of $CO_2(g)$ at 22, 50 and 85 mol% Na₂MoO₄ are in excellent agreement with the data of Shurdumov et al. ⁴⁵. At 22 mol% Na₂MoO₄, our measured liquidus temperatures were about 787°C and 768°C, respectively, in the presence and absence of $CO_2(g)$. This temperature shift of about 19°C is believed to be mainly attributed to the partial dissociation of Na₂CO_{3(S3)} to form liquid Na₂O (dissolved in the molten salt phase) and $CO_2(g)$. The calculated isobar at 1 atm is displayed in Figure 4, and shows that such a dissociation occurs. However, it is calculated to be extremely limited (mole fraction of Na₂O of the order of 10^{-8}). The calculated liquidus temperature of the (78) mol% Na₂CO₃ + 22 mol% Na₂MoO₄) binary mixture is 779°C, and becomes about 775°C if 1 mol% of Na₂CO₃ decomposes into Na₂O (dissolved in the liquid) and CO₂(g). This calculated decrease in temperature is consistent with the trend observed experimentally. When a $CO_2(g)$ saturated atmosphere was used in our DSC-TGA experiments, such a decomposition was avoided.



Figure 3 : DSC thermogram for the mixture (78 mol% Na₂CO₃ + 22 mol% Na₂MoO₄) in the presence of CO₂(g) (2nd and 3rd heating/cooling cycles only)



Figure 4 : Calculated (Na₂CO₃ + Na₂MoO₄) phase diagram in air (p(O₂) = 0.21 atm).
Experimental data from Shurdumov et al. ⁴⁵ (○) and this work (red and blue symbols) (DSC, red ● : 2nd heating without CO₂(g), blue ■ : 2nd heating with CO₂(g), red *: 3rd heating without CO₂(g), blue ◆ : 3rd heating with CO₂(g))

6.4 The $(K_2CO_3 + K_2M_0O_4)$ system

The phase diagram has been investigated by Shurdumov et al.⁴⁵ using thermal analysis. A eutectic was reported by these authors at 41.0 mol% K₂MoO₄ and 728°C. The calculated characteristics of the eutectic are 40.7 mol% K₂MoO₄ and 729°C. No solid solutions or intermediate compounds were reported. The measured limiting slope of the K2MoO4 liquidus curve agrees with equation (11), which shows that there is negligible solid solubility of K₂CO₃ in the high-temperature allotrope K₂MoO_{4(S3)}. Since no phase diagram measurements are available for K₂CO₃-rich binary mixtures, it is not known if K₂MoO₄ is partly soluble in the high-temperature allotrope K₂CO_{3(S2)}, which is present as an "endmember" in the hexagonal hP22 solid solution. By analogy with the $(Na_2CO_3 + Na_2MoO_4)$ binary system, this solid solubility was assumed to be negligible, and a constant interaction parameter of +100,000.0 J/mol was thus introduced in the model for hP22 (see Table 5). Note that K₂MoO₄ was introduced as an "end-member" in the latter model in order to reproduce its experimental solubilities in K₂SO_{4(S2)}, K₂CrO_{4(S2)} and Na₂MoO_{4(S4)} (which are all hexagonal with the P63/mmc space group), as will be discussed later in the sections devoted to the $(K_2SO_4 + K_2MoO_4)$, $(K_2CrO_4 + K_2MoO_4)$ and $(Na_2MoO_4 + K_2MoO_4)$ binary common-ion sub-systems.

A regular parameter of +100,000.0 J/mol was introduced in the oS28 solid solution in order to calculate a negligible solid solubility of K₂CO₃ in K₂MoO_{4(S2)} (see Table 5).

The calculated ($K_2CO_3 + K_2MoO_4$) phase diagram in air ($p(O_2) = 0.21$ atm) is compared to the measurements in Figure 5. According to the calculated isobar at 1 atm shown in this figure, $K_2CO_{3(S2)}$ partly decomposes into liquid K_2O (dissolved in the liquid solution) and $CO_2(g)$. Nevertheless, this decomposition is calculated to be extremely limited (mole fraction of K_2O of the order of 10^{-10}).



Figure 5 : Calculated (K₂CO₃ + K₂MoO₄) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Shurdumov et al. ⁴⁵ (●)

6.5 The $(Na_2SO_4 + Na_2MoO_4)$ system

The phase diagram has been measured by the method of cooling curves with visual readings and optical observations, ⁴⁶ and by the visual-polythermal method. ^{47, 48}

A complete solid solution at high temperatures exhibiting a minimum at about 70 mol% Na₂MoO₄ was reported by Boeke. ⁴⁶ Belyaev and Doroshenko, ⁴⁷ and Mateiko and Bukhalova ⁴⁸ also observed the existence of a complete solid solution with a minimum at 75 mol% Na₂MoO₄ and 673°C, and at 70 mol% Na₂MoO₄ and 672°C, respectively. The data of Boeke ⁴⁶ suggest in particular a small solubility of Na₂SO₄ in the low-temperature allotrope Na₂MoO₄(s₁) (see Figure 7). In this work, DSC-TGA measurements were conducted for several binary mixtures with very high concentrations of Na₂MoO₄: 90, 92, 95, 98, and 99 mol% (from 120 to 730°C). As an example, the DSC thermogram for the binary composition (5 mol% Na₂SO₄ + 95 mol% Na₂MoO₄) is shown in Figure 6.



Figure 6 : DSC thermogram for the mixture (5 mol% Na₂SO₄ + 95 mol% Na₂MoO₄) (2nd and 3rd heating/cooling cycles only)



Figure 7 : Calculated (Na₂SO₄ + Na₂MoO₄) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Boeke ⁴⁶ (○), Belyaev and Doroshenko ⁴⁷ (□), Mateiko and Bukhalova ⁴⁸ (*) and this work (blue symbols) (DSC, ◆ : average of temperatures from 2nd and 3rd heating runs). Insert: close-up of the calculated phase diagram near pure Na₂MoO₄

The calculated (Na₂SO₄ + Na₂MoO₄) phase diagram in air ($p(O_2) = 0.21$ atm) is shown along with the measurements in Figure 7.

The high-temperature allotropes $Na_2SO_{4(S2)}$ and $Na_2MoO_{4(S4)}$ have the same hexagonal crystal structure and space group P6₃/mmc (see Table 1), and therefore a high-temperature solid solution (hP22) was modeled over the entire composition range. Three interaction parameters (see Table 5) were introduced to best reproduce the experimental data of Boeke ⁴⁶ at intermediate temperatures.

Then, the liquid solution was modeled in order to reproduce our experimental hightemperature data and those of ⁴⁶⁻⁴⁸. No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the liquid phase. As seen in Table 4, the two model parameters required for the liquid have a significant amplitude. The enthalpy of mixing of the liquid calculated at 900°C (that is, above the melting temperatures of the pure salts Na₂SO₄ and Na₂MoO₄) has a minimum of about -4.45 kJ/mol. Thus, the common-cation liquid displays negative deviations from ideality. It was expected to be close to ideal owing to the close similarity of the anionic radii (2.31 Å for SO₄²⁻ and 2.33 Å for MoO₄^{2- 49}). The SO₄²⁻ and MoO₄²⁻ anions have a significant mass difference, which may lead to a substantial vibrational entropy at high temperatures. This may explain the negative deviations from ideality of the binary liquid.

In order to best reproduce our DSC-TGA measurements and the data of Boeke ⁴⁶ at low temperatures, some solid solubility of Na₂SO₄ was introduced in Na₂MoO_{4(S1)} (see the cF56 solid solution in Table 5). By analogy with the (Na₂CrO₄ + Na₂MoO₄) binary system (discussed later) for which Na₂CrO₄ is partly soluble in Na₂MoO_{4(S2)}, some solid solubility of Na₂SO₄ was also introduced in Na₂MoO_{4(S2)} (see the Na₂MoO_{4(S2)}, some solid solubility of Na₂SO₄ was also introduced in Na₂MoO_{4(S2)} (see the Na₂MoO_{4(S2)}-ss-rich solid solution in Table 5). Na₂SO_{4(S2)} and Na₂CrO_{4(S2)} have the same crystal structure and space group (see Table 1). Therefore, the Gibbs energy of the "end-member" Na₂SO₄ in the Na₂MoO_{4(S2)}-ss-rich solid solution was that of Na₂SO_{4(S2)} augmented by a positive Gibbs energy identical to that for the "end-member" Na₂CrO₄. The latter model parameter was obtained from reproduction of the available phase diagram data in (Na₂CrO₄ + Na₂MoO₄). Finally, a regular parameter of +100,000.0 J/mol was introduced in the oS28 solid solution to calculate negligible mutual solubility between Na₂MoO_{4(S3)} and

Na₂SO₄(S₃) (see Table 5).

6.6 The $(K_2SO_4 + K_2MoO_4)$ system

The phase diagram has been measured by the method of cooling curves with visual readings 50 , and by the visual-polythermal method. $^{51, 52}$ Amadori 50 reported a complete solid solution at high temperatures with a very flat minimum at about 6°C below the melting temperature of K₂MoO₄ (that is, at about 920°C). Similarly, Bergman et al. 51 , and Mateiko and Bukhalova 52 observed the formation of a complete solid solution with no marked minimum.

According to Amadori, ⁵⁰ it was difficult to measure the thermal arrests at around 450°C, and between 50 and 90 mol% K₂MoO₄. This author suggested that K₂SO₄ and K₂MoO₄ are mutually soluble at intermediate temperatures, with the formation of a continuous solid solution.

In this work, DSC-TGA measurements were performed using the NETZSCH STA 449 F1 Jupiter® instrument for several binary mixtures with various contents of K_2MoO_4 : 60, 80, and 95 mol% (from 150 to 930°C). DSC-TGA measurements were conducted using the SDT Q600 TA Instrument over the same temperature range at 70 and 80 mol% K_2MoO_4 . No systematic difference was observed between the two apparatuses, which were both used to investigate the (20 mol% K_2SO_4 + 80 mol% K_2MoO_4) mixture. As an example, the DSC thermogram for the binary composition (30 mol% K_2SO_4 + 70 mol% K_2MoO_4) is displayed in Figure 8.



Figure 8 : DSC thermogram for the mixture (30 mol% K₂SO₄ + 70 mol% K₂MoO₄) (2nd and 3rd heating/cooling cycles only)

The calculated ($K_2SO_4 + K_2MoO_4$) phase diagram in air ($p(O_2) = 0.21$ atm) is compared to the measurements in Figure 9. This phase diagram displays four different solid solutions : a high-temperature hexagonal solid solution (hP22) rich in $K_2SO_{4(S2)}$ and existing over a large composition range, a high-temperature trigonal solid solution ($K_2MoO_{4(S3)}$ -ht-ss) rich in $K_2MoO_{4(S3)}$ and diluted in K_2SO_4 , an orthorhombic low-temperature solid solution (oP28) rich in $K_2SO_{4(S1)}$ and diluted in K_2MoO_4 , and an orthorhombic low-temperature solid solution (oS28) rich in $K_2MoO_{4(S2)}$ and diluted in K_2SO_4 .

The high-temperature allotropes $K_2SO_{4(S2)}$ (hexagonal, P6₃/mmc) and $K_2MoO_{4(S3)}$ (trigonal, P $\overline{3}$ m1) do not have the same crystal structure (see Table 1). Therefore, two terminal solid solutions (hP22 and $K_2MoO_{4(S3)}$ -ht-ss) were introduced at high temperatures. The hP22 solid solution was first modeled to best reproduce the low-temperature data of Amadori; ⁵⁰ two interaction parameters were required (see Table 5).

Simultaneously, some solubility of K_2MoO_4 in $K_2SO_{4(S1)}$ (oP28 solid solution) was introduced in order to improve the agreement between our calculations and the corresponding measurements ⁵⁰ for K_2SO_4 -rich mixtures. Note that $K_2SO_{4(S1)}$ and $K_2CrO_{4(S1)}$ are mutually soluble in oP28. The Gibbs energy of the "end-member" K_2MoO_4 in oP28 was selected in this work to best reproduce simultaneously the ($K_2SO_4 + K_2MoO_4$) and ($K_2CrO_4 + K_2MoO_4$) experimental phase diagrams. (The latter system will be discussed later). Once the hP22 solid solution was optimized, the ($K_2SO_4 + K_2MoO_4$) liquid was modeled in order to best reproduce the high-temperature measurements. The $K_2MoO_{4(S3)}$ -ht-ss solid solution was then modeled; the maximum solubility of K_2SO_4 in $K_2MoO_{4(S3)}$ was arbitrarily set to about 6 mol%.

Finally, some solubility of K_2SO_4 in $K_2MoO_{4(S2)}$ (oS28 solid solution) was introduced to best reproduce the low-temperature thermal arrest of Amadori ⁵⁰ at 93.3 mol% K_2MoO_4 along with our low-temperature DSC thermal arrest at 95 mol% K_2MoO_4 .

The Gibbs energy of the "end-member" K_2SO_4 in the oS28 solid solution was previously obtained by Lindberg et al. ¹⁴ upon optimization of the ($K_2SO_4 + Na_2SO_4$) binary system. A very negative (-26,000.0 J/mol) constant Redlich-Kister interaction parameter had to be introduced by us between K_2SO_4 and K_2MoO_4 in the oS28 solid solution (see Table 5).

No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the ($K_2SO_4 + K_2MoO_4$) liquid phase. As seen in Table 4, this common-cation binary liquid exhibits small positive deviations from ideality. It was expected to be close to ideal owing to the very close similarity of the radii of the SO₄²⁻ and MoO₄²⁻ anions. ⁴⁹



Figure 9 : Calculated (K₂SO₄ + K₂MoO₄) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Amadori ⁵⁰ (^O), Bergman et al. ⁵¹ ([□]), Mateiko and Bukhalova ⁵² ([◊]), and this work (blue symbols) (DSC using the NETZSCH STA 449 F1 Jupiter[®] instrument // [●] : 2nd heating, [♦] : 3rd heating; DSC using the SDT Q600 TA Instrument // [■] : average of temperatures from 2nd and 3rd heating runs)

6.7 The $(Na_2CrO_4 + Na_2MoO_4)$ system

The phase diagram has been measured by visual observation with a Pt/Pt-Rh thermocouple and a sensitive millivoltmeter. ⁴⁸ Mateiko and Bukhalova ⁴⁸ reported a complete solid solution at high temperatures with no minimum.

In this work, DSC-TGA measurements were conducted for several binary mixtures with various contents of Na_2MoO_4 : 10 mol% (from 200 to 790°C), 30 and 50 mol% (from 200 to 765°C), and 70 and 90 mol% (from 200 to 725°C).

As an example, the DSC thermogram for the binary composition ($10 \mod \% Na_2CrO_4 + 90 \mod \% Na_2MoO_4$) is shown in Figure 10.



Figure 10 : DSC thermogram for the mixture (10 mol% Na₂CrO₄ + 90 mol%

Na₂MoO₄) (2nd and 3rd heating/cooling cycles only)

The calculated (Na₂CrO₄ + Na₂MoO₄) phase diagram in air ($p(O_2) = 0.21$ atm) is shown along with the measurements in Figure 11. This phase diagram exhibits four different solid solutions : a high-temperature hexagonal solid solution (hP22) existing over the entire composition range (owing to the fact that Na₂CrO₄(S₂) and Na₂MoO₄(S₄) are both hexagonal with the space group P6₃/mmc as seen in Table 1), an orthorhombic low-temperature solid solution (oS28) rich in Na₂CrO₄(S₁) and diluted in Na₂MoO₄, an intermediate-temperature orthorhombic solid solution (Na₂MoO₄(S₂)-ss-rich) rich in Na₂MoO₄(S₂) and diluted in Na₂CrO₄, and a cubic low-temperature solid solution (cF56) rich in Na₂MoO₄(S₁) and diluted in Na₂CrO₄.

Those four solid solutions were modeled simultaneously to best reproduce our lowtemperature DSC thermal arrests. Two positive interaction parameters were required for hP22. The Gibbs energy of the "end-member" Na₂CrO₄ in the Na₂MoO_{4(S2)}-ss-rich solid solution was selected to best reproduce our DSC data at 50, 70 and 90 mol% Na₂MoO₄. Then, by analogy with the $(Na_2SO_4 + Na_2MoO_4)$ binary system (previously discussed) for which Na₂SO₄ is partly soluble in Na₂MoO_{4(S1)}, some solid solubility of Na₂CrO₄ was introduced in Na₂MoO_{4(S1)} (see the cF56 solid solution in Table 5). Na₂SO_{4(S1)} and Na₂CrO_{4(S1)} have the same crystal structure and space group (see Table 1). Therefore, the Gibbs energy of the "end-member" Na₂CrO₄ in the cF56 solid solution was that of $Na_2CrO_{4(S1)}$ augmented by a positive Gibbs energy identical to that for the "end-member" Na₂SO₄, which was obtained from the low-temperature data of Boeke 46 in (Na₂SO₄ + Na₂MoO₄). The oS28 solid solution was then modeled to best reproduce our lowtemperature DSC measurements at 10 and 30 mol% Na2MoO4. For the first composition, an intense peak was observed at about 406°C while a low intensity peak was measured at about 446°C. As seen in Figure 11, the former temperature is satisfactorily reproduced by our model.

The $(Na_2CrO_4 + Na_2MoO_4)$ liquid phase was modeled to best reproduce the hightemperature phase equilibria. Again, no enthalpy of mixing or activity data were available to calibrate the liquid. As seen in Table 4, the three optimized model parameters are not large. The enthalpy of mixing of the liquid calculated at 800°C (that is, above the melting temperatures of the pure salts Na₂CrO₄ and Na₂MoO₄) is always positive, with a maximum value of about 0.84 kJ/mol. The common-cation liquid thus displays small positive deviations from ideality. It was expected to be close to ideal due to the very close similarity of the anionic radii (2.32 Å for CrO_4^{2-} , and 2.33 Å for MoO_4^{2-49}).

A regular parameter of +100,000.0 J/mol was introduced in the oF56 solid solution in order to calculate a negligible solid solubility of Na₂CrO₄ in Na₂MoO_{4(S3)} (see Table 5).



Figure 11 : Calculated (Na₂CrO₄ + Na₂MoO₄) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Mateiko and Bukhalova ⁴⁸ (□) and this work (blue symbols) (DSC, blue [○] : 2nd heating, blue [◆] : 3rd heating)

6.8 The $(K_2CrO_4 + K_2M_0O_4)$ system

The phase diagram has been measured by the method of cooling curves with visual readings, ⁵⁰ and the visual-polythermal method. ⁵² A complete solid solution was reported at high temperatures, without any marked minimum. ⁵²

According to Amadori, ⁵⁰ owing to the large mutual solubility existing between K₂CrO₄

and K_2MoO_4 at 25°C, a complete solid solution is likely to exist between $K_2CrO_{4(S1)}$ and $K_2MoO_{4(S2)}$ at 450°C, with the presence of a minimum in the range of 65 to 100 mol% K_2MoO_4 .

In the present work, DSC-TGA measurements were performed for several binary mixtures with various contents of K_2MoO_4 : 75, 85, and 95 mol% (from 200 to 965°C). As an example, the DSC thermogram for the binary composition (15 mol% K_2CrO_4 + 85 mol% K_2MoO_4) is displayed in Figure 12.





Figure 12 : DSC thermogram for the mixture (15 mol% K₂CrO₄ + 85 mol% K₂MoO₄) (2nd and 3rd heating/cooling cycles only)

The calculated ($K_2CrO_4 + K_2MoO_4$) phase diagram in air ($p(O_2) = 0.21$ atm) is compared to the measurements in Figure 13. Its morphology is very similar to that of the ($K_2SO_4 + K_2MoO_4$) phase diagram discussed previously. There are four different solid solutions: a high-temperature hexagonal solid solution (hP22) rich in $K_2CrO_{4(S2)}$ and existing over a large composition range, a high-temperature trigonal solid solution ($K_2MoO_{4(S3)}$ -ht-ss) rich in $K_2MoO_{4(S3)}$ and diluted in K_2CrO_4 , an orthorhombic low-temperature solid solution (oP28) rich in $K_2CrO_{4(S1)}$ and diluted in K_2MoO_4 , and an orthorhombic low-temperature solid solution (oS28) rich in $K_2MoO_{4(S2)}$ and diluted in K_2CrO_4 . Since the high-temperature allotropes $K_2CrO_{4(S2)}$ (hexagonal, P6₃/mmc) and $K_2MoO_{4(S3)}$ (trigonal, P3m1) do not have the same crystal structure (see Table 1), two terminal solid solutions (hP22 and $K_2MoO_{4(S3)}$ -ht-ss) were considered at high temperatures.

The hP22 solid solution was first modeled to best reproduce the low-temperature data of Amadori ⁵⁰ and our low-temperature DSC thermal arrest at 75 mol% K₂MoO₄; three positive interaction parameters were necessary (see Table 5). Some solubility of K₂MoO₄ in K₂CrO_{4(S1)} (oP28 solid solution) was introduced to improve the agreement between our calculations and the data of Amadori ⁵⁰ for K₂CrO₄-rich mixtures. As explained previously, the Gibbs energy of the "end-member" K₂MoO₄ in oP28 was obtained by optimizing simultaneously the (K₂CrO₄ + K₂MoO₄) and (K₂SO₄ + K₂MoO₄) phase diagrams. The K₂MoO_{4(S3)}-ht-ss solid solution was then modeled to best reproduce our low-temperature DSC thermal arrest at 85 mol% K₂MoO₄.

Once the hP22 solid solution was optimized, the ($K_2CrO_4 + K_2MoO_4$) liquid was modeled in order to best reproduce the available high-temperature phase equilibria. No enthalpy of mixing or activity data were available to calibrate the liquid. As seen in Table 4, it exhibits positive deviations from ideality. The enthalpy of mixing of the liquid calculated at 1000°C (that is, above the temperatures of fusion of K_2CrO_4 and K_2MoO_4) has a maximum value of about 1.75 kJ/mol. The common-cation liquid was expected to be somewhat closer to ideal owing to the very close similarity of the radii of the CrO_4^{2-} and MoO_4^{2-} anions.⁴⁹ Finally, some solubility of K_2CrO_4 in $K_2MoO_{4(S2)}$ (oS28 solid solution) was introduced to

Finally, some solubility of K₂CrO₄ in K₂MoO_{4(S2)} (0S28 solid solution) was introduced to best reproduce the low-temperature measurement of Amadori ⁵⁰ and our low-temperature DSC thermal arrest at 95 mol% K₂MoO₄. The Gibbs energy of the "end-member" K₂CrO₄ in the oS28 solid solution was previously selected by us ¹⁶ upon optimization of the (K₂CrO₄ + Na₂CrO₄) binary system (K₂MoO_{4(S2)} and Na₂CrO_{4(S1)} are mutually soluble). In this work, a very negative (-19,500.0 J/mol) constant Redlich-Kister interaction parameter had to be introduced between K₂CrO₄ and K₂MoO₄ in the oS28 solid solution (see Table 5).



Figure 13: Calculated (K₂CrO₄ + K₂MoO₄) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Amadori ⁵⁰ ([○]), Mateiko and Bukhalova ⁵² ([□]) and this work (blue symbols) (DSC, blue • : average of temperatures from 2nd and 3rd heating runs)

6.9 The $(Na_2MoO_4 + K_2MoO_4)$ system

Several studies have been performed on the $(Na_2MoO_4 + K_2MoO_4)$ binary phase diagram. ^{44, 53-55} Amadori ⁵⁴ used the method of cooling curves with visual readings, while Belyaev and Sholokhovich ⁵³ used the visual-polythermal method. The latter authors reported the formation of a complete solid solution at high temperatures, with the presence of a minimum at around 21 mol% K₂MoO₄ and 656°C. According to Amadori, ⁵⁴ two terminal solid solutions (based on the high-temperature allotropes of Na₂MoO₄ and K₂MoO₄) were formed at high temperatures, and the intermediate compound Na₂MoO₄.K₂MoO₄ was formed upon cooling.

Using the visual-polythermal method, Bukhalova and Mateiko⁴⁴ observed a eutectic at 19 mol% K₂MoO₄ and 667°C, and also two transition points at 37 mol% K₂MoO₄ and 686°C,

and at 54 mol% K_2MoO_4 and 737°C, respectively. They suggested the formation of two intermediate compounds (Na₂MoO₄.K₂MoO₄ and Na₂MoO₄.2K₂MoO₄) melting incongruently.

Ding et al. ⁵⁵ conducted DTA and XRD measurements at both low and high temperatures. In particular, they investigated by XRD two (Na₂MoO₄ + K₂MoO₄) binary mixtures at 50 and 66.7 mol% K₂MoO₄, and the high-temperature allotropes of Na₂MoO₄ and K₂MoO₄. They ruled out the eutectic and the two intermediate compounds reported by Bukhalova and Mateiko. ⁴⁴ According to Ding et al. ⁵⁵, the visual-polythermal method used by Bukhalova and Mateiko to identify incongruently melting compounds cannot provide reliable results.

The calculated (Na₂MoO₄ + K₂MoO₄) phase diagram in air ($p(O_2) = 0.21$ atm) is shown along with the measurements in Figure 14. This phase diagram displays five different solid solutions : a high-temperature hexagonal solid solution (hP22) rich in Na₂MoO_{4(S4)} and existing over a large composition range, a high-temperature trigonal solid solution (K₂MoO_{4(S3)}-ht-ss) rich in K₂MoO_{4(S3)} and diluted in Na₂MoO₄, an intermediatetemperature orthorhombic solid solution (oF56) rich in Na₂MoO_{4(S3)} and diluted in K₂MoO₄, a low-temperature orthorhombic solid solution (oS28) rich in K₂MoO_{4(S2)} and diluted in Na₂MoO₄, and the non-stoichiometric phase K₃Na(MoO₄)₂ (molybdenumglaserite, hP14). These various solid solutions and the optimized model parameters are described in detail in Table 5.



Figure 14: Calculated (Na2MoO4 + K2MoO4) phase diagram in air (p(O2) = 0.21 atm). Experimental data from Amadori ⁵⁴ (⊕), Belyaev and Sholokhovich ⁵³ (△),
Bukhalova and Mateiko ⁴⁴ (○) , Ding et al. ⁵⁵ (*), Fabry et al. ⁴⁰ (◇) and this work (red and blue symbols) (DSC , red ▲ : 1st heating for molybdenum-glaserite equilibrated at 400°C for 4 weeks, red ▲ : 2nd heating for molybdenum-glaserite equilibrated at 400°C for 4 weeks, red ▲ : 3rd heating for molybdenum-glaserite equilibrated at 400°C for 4 weeks, blue ⊕ : 2nd heating for molybdenum-glaserite equilibrated at 400°C for 4 weeks, blue ⊕ : 2nd heating for molybdenum-glaserite equilibrated at 400°C for 4 weeks, blue ⊕ : 2nd heating for mechanical mixtures of pre-treated reagents, blue ■ : 3rd heating for mechanical mixtures of pre-treated reagents)

Ding et al. ⁵⁵ claimed that the high temperature allotropes of Na₂MoO₄ and K₂MoO₄ are isomorphic (i.e. same crystal structure and space group). However, based on our previous work, ⁴ Na₂MoO_{4(S4)} (hexagonal, P6₃/mmc) and K₂MoO_{4(S3)} (trigonal, P $\overline{3}$ m1) do not have the same crystal structure (see Table 1). Therefore, two terminal solid solutions (hP22 and K₂MoO_{4(S3)}-ht-ss) were modeled at high temperatures in the present work.

For the molybdenum-glaserite phase $K_3Na(MoO_4)_2$, a solid-solid transition occurs at 513K ⁴⁰ between a stoichiometric compound (monoclinic, space group C2/c), which is stable at

room temperature, and a non-stoichiometric phase (trigonal, $P\overline{3}m1$). ^{40, 56} There is some similarity with cryolite (Na₃AlF₆), for which a solid-solid transition occurs at about 834K between a stoichiometric compound (monoclinic, space group P2₁/n) and a non-stoichiometric phase (cubic, space group Fm3m). ⁵⁷

As shown in Table 5, the high-temperature non-stoichiometric glaserite phase (hP14) was modeled with the following sublattice structure : $(K^+, Na^+)_3(Na^+)(SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-})_2$. The sulfur-glaserite ¹⁴ and chrome-glaserite ¹⁶ phases were modeled previously, and the corresponding model parameters were used directly in this work. To model the molybdenum-glaserite phase, the two new "end-members" K₃Na(MoO₄)₂ and Na₃Na(MoO₄)₂ were added in the existing hP14 solid solution. Their Gibbs energies were the only model parameters. That is, no interaction parameters were required in this work. To our knowledge, the enthalpy change for the solid-solid transition between the two forms of molybdenum-glaserite has not been measured. As a first approximation, the corresponding entropy change was estimated as half that for the transition Na₂MoO_{4(S1)} = Na₂MoO_{4(S2)} plus 1.5 times that for the transition K₂MoO_{4(S1)} = K₂MoO_{4(S2)}. Note that the temperatures and enthalpy changes for these two solid-solid transitions were directly taken from our previous study. ⁴

The enthalpy change for the solid-solid transition of $K_3Na(MoO_4)_2$ was estimated as 21,733.4 J/mol at 513K. The low-temperature stoichiometric compound $K_3Na(MoO_4)_2$ was introduced in this work. Its Gibbs energy was estimated by starting with a Gibbs energy of formation from the pure end-members $[0.5 Na_2MoO_{4(S1)} + 1.5 K_2MoO_{4(S1)} = K_3Na(MoO_4)_{2(S)}]$ equal to zero. Then, $\Delta H^{\circ}_{298.15 \text{ K}}$ and $S^{\circ}_{298.15 \text{ K}}$ were adjusted to best reproduce the experimental temperature ⁴⁰ and assessed enthalpy change for the solid-solid transition of molybdenum-glaserite. The reactions $0.055 Na_2MoO_{4(S1)} + 0.945 K_3Na(MoO_4)_{2(S)} = 0.973 \text{ hP14}$ and $K_3Na(MoO_4)_{2(S)} = 0.961 \text{ hP14} + 0.079 K_2MoO_{4(S1)}$ were calculated at 239°C (enthalpy change of 21,746 J/mol) and 244°C (enthalpy change of 20,346 J/mol), respectively.

The optimized thermodynamic properties $(\Delta H^{\circ}_{298.15 \text{ K}}, S^{\circ}_{298.15 \text{ K}}, \text{ and } C_P)$ of the stoichiometric compound K₃Na(MoO₄)₂ are given in Table 2. The Open Quantum Materials Database (OQMD) ^{58, 59} reported an enthalpy of formation at 0 K of -3,139,247 J/mol derived from Density Functional Theory (DFT) calculations. The corresponding

value given in Materials Project ⁶⁰ is -2,955,539 J/mol.

In this work, DSC-TGA measurements were conducted for mechanical mixtures of the pretreated reagents Na₂MoO₄ and K₂MoO₄. Nine different binary mixtures with various contents of K₂MoO₄ were investigated : 5, 15, 30, 40 and 50 mol% (from 45 to 750°C), 65 mol% (from 45 to 860°C), 80 mol% (from 45 to 890°C), and 90 and 95 mol% (from 45 to 950°C). In addition, DSC-TGA measurements were performed for the molybdenumglaserite composition of (35 mol% Na₂MoO₄ + 65 mol% K₂MoO₄) equilibrated at 400°C for four weeks, to which an excess of Na₂MoO₄ or K₂MoO₄ was added subsequently. Two binary mixtures at 62.5 and 70 mol% K₂MoO₄ were studied under those conditions, from 180 to 840°C. All measured thermal arrests are listed in the Supporting Information (see Tables S8 and S9). As an example, the DSC thermogram for the mechanical mixture (70 mol% Na₂MoO₄ + 30 mol% K₂MoO₄) is displayed in Figure 15.



Figure 15 : DSC thermogram for the mixture (70 mol% Na₂MoO₄ + 30 mol% K₂MoO₄) (2nd and 3rd heating/cooling cycles only)

No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the (Na₂MoO₄ + K₂MoO₄) liquid phase. First, a constant parameter of -1,419.6 J/mol was used by analogy with the (Na₂SO₄ + K₂SO₄)¹⁴ and (Na₂CrO₄ + K₂CrO₄)¹⁶ liquid

phases, which were modeled previously. However, it was not possible to obtain a set of parameters for the five solid solutions permitting the calculation of a satisfactory phase diagram. Finally, two model parameters (including one composition-dependent parameter) were used for the (Na₂MoO₄ + K₂MoO₄) liquid (see Table 4). The enthalpy of mixing of the liquid calculated at 950°C (that is, above the temperatures of fusion of Na₂MoO₄ and K₂MoO₄) has a minimum value of about -0.28 kJ/mol, which is reasonable. The common-anion liquid was expected to be close to ideal owing to the similarity of the radii of the Na⁺ and K⁺ cations. ⁶¹

Then, the hexagonal solid solution (hP22) was modeled in order to best reproduce the hightemperature measurements (i.e. phase equilibria with the liquid solution) and the maximum extension of the molybdenum-glaserite phase (hP14) at about 646°C and 65.5 mol% K_2MoO_4 . Only one positive model parameter was required for hP22, and the Gibbs energies of the two "end-members" K₃Na(MoO₄)₂ and Na₃Na(MoO₄)₂ in hP14 were optimized simultaneously. To model the oF56 solid solution, the data of Ding et al. ⁵⁵ were favoured, and four model parameters were used : two parameters (including one temperature-dependent parameter) for the Gibbs energy of the "end-member" K₂MoO₄, and two Redlich-Kister interaction parameters. As seen in Figure 14, the calculated extent of oF56 is reasonable, and the eutectoid reaction hP22 = oF56 + hP14 is calculated at about 36.8 mol% K₂MoO₄ and 461°C. Finally, the K₂MoO_{4(S3)}-ht-ss and oS28 solid solutions were modeled to best reproduce, respectively, the high-temperature and low-temperature measurements of Amadori ⁵⁴ and Ding et al. ⁵⁵ The maximum solubility of Na₂MoO₄ in K₂MoO_{4(S3)} was arbitrarily set to about 4.3 mol%.

6.10 The $(K_2Cr_2O_7 + K_2Mo_2O_7)$ system

The phase diagram has been measured by Amadori ⁶² using the method of cooling curves with visual readings, and a complete solid solution was reported at high temperatures. The calculated ($K_2Cr_2O_7 + K_2Mo_2O_7$) phase diagram in air ($p(O_2) = 0.21$ atm) is compared to the measurements in Figure 16.

To our knowledge, there are no enthalpy of mixing or activity data to calibrate the liquid

solution. The latter was assumed to be ideal (that is, $\Delta g_{K_2/(Cr_2O_7)(Mo_2O_7)} = 0$) owing to the expected similarity of the radii of the anions $Cr_2O_7^{2-}$ and $Mo_2O_7^{2-}$. As seen in Table 1, the high-temperature allotropes $K_2Cr_2O_{7(S2)}$ and $K_2Mo_2O_{7(S2)}$ are both monoclinic with the space group P2₁/c. Therefore, a high-temperature solid solution ($K_2Cr_2O_7(s.s)$) was introduced over the entire composition range. One positive regular parameter was used to reproduce the experimental solidus of Amadori ⁶² from 0 to about 90 mol% K₂Mo₂O₇. Amadori reported for K₂Mo₂O₇ a melting temperature about 14°C lower than our selected value, which was based on the available data from the literature ¹⁷. Hence, it was not possible to reproduce the experimental solidus of Amadori ⁶² above 90 mol% K₂Mo₂O₇. The low-temperature allotropes K₂Cr₂O₇(s₁) and K₂Mo₂O₇(s₁) are both triclinic with the space group P1 (see Table 1). Thus, a low-temperature solid solution (aP44) was modeled over the entire composition range. Owing to the lack of relevant phase diagram data, as a first approximation, a regular parameter identical to that in the K₂Cr₂O₇(s.s) solid solution was used.



Figure 16 : Calculated (K₂Cr₂O₇ + K₂Mo₂O₇) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Amadori ⁶² (●)

6.11 The $(Na_2MoO_4 + Na_2Mo_2O_7)$ system

The (Na₂MoO₄ + MoO₃) phase diagram has been measured by thermal analysis ^{63, 64} and DTA. ⁶⁵ The relevant compositions were expressed in terms of the (Na₂MoO₄ + Na₂Mo₂O₇) binary sub-system. These various authors reported a eutectic at 37.0 mol% Na₂Mo₂O₇ and 551°C, 35.1 mol% Na₂Mo₂O₇ and 556°C, and 25.0 mol% Na₂Mo₂O₇ and 559°C, respectively. The calculated characteristics of the eutectic are 35.4 mol% Na₂Mo₂O₇ and 555°C. Using thermal analysis, Mokhosoev and Fedorov ⁶⁶ measured the (Na₂Mo₂O₇ + Na₂CO₃) phase diagram, and claimed that "this system can be represented as two binary systems : (Na₂Mo₂O₇ + Na₂MoO₄) and (Na₂MoO₄ + Na₂CO₃)". Measurements were provided graphically for the (Na₂Mo₂O₇ + Na₂MoO₄) phase diagram, and a eutectic was reported at 40.0 mol% Na₂Mo₂O₇ and 538°C.

The calculated (Na₂MoO₄ + Na₂Mo₂O₇) phase diagram in air (p(O₂) = 0.21 atm) is shown along with the measurements in Figure 17. The data of Mokhosoev and Fedorov ⁶⁶ were discarded since it is not clear how they were obtained. Also, the corresponding experimental liquidus of Na₂Mo₂O₇ substantially disagrees with those of the other studies. ⁶³⁻⁶⁵ The measurements of Groschuff ⁶³ were favoured in this work since, at the same time, this author obtained satisfactory data for the (K₂CrO₄ + K₂Cr₂O₇) phase diagram. ¹⁶ As seen in Table 4, one of the two model parameters required for the (Na₂MoO₄ + Na₂Mo₂O₇) liquid has a significant amplitude. The enthalpy of mixing of the liquid calculated at 700°C (that is, above the melting temperatures of the pure salts Na₂MoO₄ and Na₂Mo₂O₇) has a maximum of about 1.07 kJ/mol. Thus, the common-cation liquid exhibits positive deviations from ideality. It was expected to be relatively close to ideal owing to the similarity of the two anions.



Figure 17 : Calculated (Na2MoO₄ + Na2Mo2O₇) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Groschuff ⁶³ (▼), Hoermann ⁶⁴ (≭), Caillet ⁶⁵ (○), and Mokhosoev and Fedorov ⁶⁶ (△)

6.12 The $(K_2M_0O_4 + K_2M_0_2O_7)$ system

The (K₂MoO₄ + MoO₃) phase diagram has been measured by thermal analysis ^{64, 67} and DTA. ⁶⁵ The relevant compositions were expressed in terms of the (K₂MoO₄ + K₂Mo₂O₇) binary sub-system. Amadori ⁶⁷ and Caillet ⁶⁵ reported a eutectic at 475-480°C, and 61.3 mol% K₂Mo₂O₇ and 480°C, respectively. The calculated (K₂MoO₄ + K₂Mo₂O₇) phase diagram in air (p(O₂) = 0.21 atm) is compared to the measurements in Figure 18. The (K₂MoO₄ + K₂Mo₂O₇) binary liquid was assumed to be ideal (that is, $\Delta g_{K_2/(MoO_4)(Mo_2O_7)} = 0$). Under those conditions, the experimental liquiduses of K₂MoO₄ from Amadori ⁶⁷ and Hoermann ⁶⁴ are satisfactorily reproduced by the model up to about 80 mol% K₂Mo₂O₇. The calculated characteristics of the eutectic are 88.3 mol% K₂Mo₂O₇ and 484°C. The latter is close to the measured eutectic temperatures of Amadori ⁶⁷ and Caillet. ⁶⁵



Figure 18: Calculated (K₂MoO₄ + K₂Mo₂O₇) phase diagram in air (p(O₂) = 0.21 atm). Experimental data from Amadori ⁶⁷ (\triangle), Hoermann ⁶⁴ (%), and Caillet ⁶⁵ (\bigcirc)

7. Molybdate-based common-cation ternary sub-systems : (Na₂SO₄+ Na₂CrO₄+ Na₂MoO₄)

To our knowledge, experimental data are available only for the $(Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4)$ sub-system. The liquidus surface of this system was investigated by Mateiko and Bukhalova ⁴⁸ using visual observations. Six isoplethal sections were measured. The calculated liquidus projection is shown in Figure 19; the hexagonal solid solution hP22 precipitates from the liquid phase over the entire composition range. As an example, three calculated isoplethal sections are compared to the available data in Figures 20 to 22. The remaining three isoplethal sections are given in the Supplementary Information (see Figures S2 to S4). No ternary excess parameter was included for the liquid phase. That is, calculations were made using solely the optimized model parameters for the three

common-cation binary sub-systems. The $(Na_2SO_4 + Na_2CrO_4)$ binary sub-system was modeled previously, ¹⁶ and the corresponding model parameters were used directly in this work. Measurements in Figures 20, 22, S2 and S4 agree better with the calculated liquidus whereas data in Figure 21 agree better with the calculated solidus. Overall, agreement between the calculations and the measurements of Mateiko and Bukhalova ⁴⁸ is satisfactory.



Figure 19 : Calculated liquidus projection of the (Na₂SO₄ + Na₂CrO₄ + Na₂MoO₄) system



Figure 20 : Calculated isoplethal section in the (Na₂SO₄ + Na₂CrO₄ + Na₂MoO₄) system ((Na₂CrO₄)_{0.5}(Na₂MoO₄)_{0.5}-Na₂SO₄). Experimental data from Mateiko and Bukhalova ⁴⁸ (●) and this work (blue symbols) (DSC, blue [○] : 2nd heating, blue ◆ : 3rd heating)



Figure 21 : Calculated isoplethal section in the (Na₂SO₄ + Na₂CrO₄ + Na₂MoO₄)



system ((Na2SO4)0.5(Na2MoO4)0.5-Na2CrO4). Experimental data from Mateiko and Bukhalova ⁴⁸ (•)

Figure 22 : Calculated isoplethal section in the (Na₂SO₄ + Na₂CrO₄ + Na₂MoO₄) system ((Na₂SO₄)_{0.3}(Na₂MoO₄)_{0.7}-Na₂CrO₄). Experimental data from Mateiko and Bukhalova ⁴⁸ (♥)

8. Molybdate-based ternary reciprocal sub-systems : (NaCl + KCl + Na2MoO4 + K2MoO4)

To our knowledge, experimental data are available only for the $(NaCl + KCl + Na_2MoO_4 + K_2MoO_4)$ sub-system. Seventeen isoplethal sections (including the $(K_2MoO_4 + Na_2Cl_2)$ and $(Na_2MoO_4 + K_2Cl_2)$ diagonal sections) were measured by Bukhalova and Mateiko⁴⁴ using the visual-polythermal method. In each case, a pure salt was added to a common-cation or common-anion binary mixture. The calculated liquidus projection of this system is displayed in Figure 23. In the reciprocal square in this figure, the four apices correspond to the pure salts: NaCl, KCl, Na₂MoO₄, and K₂MoO₄. The compositions are expressed in

terms of cationic and anionic equivalent fractions to ensure that tie-lines are straight lines. The *X*-axis corresponds to the cationic molar ratio $n_K/(n_{Na} + n_K)$ while the *Y*-axis corresponds to the anionic molar ratio $n_{Cl}/(n_{Cl} + 2n_{MoO_4})$. A small ternary reciprocal parameter was introduced for the liquid phase (see Table 4). The (NaCl + KCl) common-anion binary sub-system was modeled previously, ¹⁹ and the corresponding model parameters were used directly in this work.

As an example, five calculated isoplethal sections are compared to the available measurements in Figures 24 to 28. The remaining twelve isoplethal sections are given in the Supplementary Information (see Figures S5 to S16). In these various figures, the filled circles refer to the original data while the empty circles refer to interpolated liquidus temperatures that were determined from the intersections with other sections. In most cases, these two series of symbols agreed well, and thus no major inconsistency was detected in the reported data of Bukhalova and Mateiko. ⁴⁴ Overall, agreement between the calculations and the available measurements is satisfactory.

In Figures 24, 26, S5, S6, S9, S10, S15 and S16, a solid-solid miscibility gap, which can be attributed to the (NaCl + KCl) solid solution (cF8), is calculated at low temperatures (below 500°C).



Figure 23 : Calculated liquidus projection of the (NaCl + KCl + Na₂MoO₄ +



Figure 24: Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system (Na₂Cl₂-K₂MoO₄). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko ⁴⁴ (ullet, \bigcirc)



Figure 25 : Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄)

system (K₂Cl₂-Na₂MoO₄). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).



Experimental data from Bukhalova and Mateiko ⁴⁴ (ullet, \bigcirc)

Figure 26 : Calculated isoplethal section in the (NaCl + KCl + Na2MoO₄ + K2MoO₄) system ((Na2Cl2)0.75(K2Cl2)0.25-K2MoO₄). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter). Experimental data from Bukhalova and Mateiko ⁴⁴ (●, ○)



Figure 27: Calculated isoplethal section in the (NaCl + KCl + Na2MoO₄ + K2MoO₄)
system ((Na2MoO₄)0.85(K2MoO₄)0.15-K2Cl2). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter). Experimental data from Bukhalova and Mateiko ⁴⁴ (●, ○)



Figure 28 : Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system ((K₂Cl₂)_{0.35}(K₂MoO₄)_{0.65}-Na₂MoO₄). Black lines: final calculations (with one

ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter). Experimental data from Bukhalova and Mateiko ⁴⁴ (●, ○)

9. Multicomponent system (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂MoO₄ + Na₂Mo₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇ + K₂O) (diluted in free oxides)

The MQMQA described in section 3 was used for the liquid phase of the 18-component system (diluted in free oxides). Phase diagram data were very limited for Na₂MoO₄- and K₂MoO₄-containing ternary common-cation sub-systems, ternary reciprocal sub-systems (i.e. systems with Na, K, and two anions) and higher-order sub-systems. Satisfactory predictions were obtained in the $(Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4)$ system, whereas one small ternary reciprocal parameter was required for the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system. In our previous work, ¹⁶ satisfactory predictions were obtained in the $(KCl + K_2CO_3 + K_2CrO_4), (Na_2CO_3 + Na_2SO_4 + Na_2CrO_4), (Na_2SO_4 + K_2SO_4 + Na_2CrO_4)$ $+ K_2CrO_4$), and (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) systems, while one small ternary excess parameter and three small ternary reciprocal parameters were necessary for the $(K_2CO_3 + K_2SO_4 + K_2CrO_4)$ and $(Na_2CO_3 + K_2CO_3 + Na_2CrO_4 + K_2CrO_4)$ systems, respectively. For all ternary and ternary reciprocal sub-systems evaluated in the present work and previously, ^{14-16, 20} no, or only small, ternary or ternary reciprocal excess parameters were necessary to reproduce the available experimental data. Therefore, assuming that ternary or ternary reciprocal excess parameters can be neglected for all ternary and ternary reciprocal sub-systems for which data are lacking is expected to lead to accurate predictions of the 18-component liquid phase (diluted in free oxides).

Various multicomponent solid solutions (hP22, oS28, oP28, hP14, oF56, cF56, $K_2MoO_{4(S3)}$ -ht-ss, Na₂MoO_{4(S2)}-ss-rich, $K_2Cr_2O_7(s.s)$, aP44 and aP22) were modeled in this study and previously ^{14-16, 20} using the MQMQA for hP22 and the CEF described in section 4 for all other solid solutions. In the present work, experimental phase equilibria involving hP22, hP14 and $K_2MoO_{4(S3)}$ -ht-ss were satisfactorily reproduced in the (Na₂SO₄+Na₂CrO₄

+ Na₂MoO₄) and (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) systems without introducing any additional parameters in the models for those solid solutions. Similarly, in our previous work, ¹⁶ measured phase equilibria involving hP22, hP14 and oP28 were satisfactorily reproduced in the (Na₂SO₄ + K₂SO₄ + Na₂CrO₄ + K₂CrO₄) and (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) systems without any additional parameters. Therefore, the developed thermodynamic model is expected to predict accurately phase equilibria in the multicomponent system.

10. Conclusions

A thorough critical evaluation of all available phase diagram and thermodynamic data for all condensed phases of the (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂MoO₄ + Na₂Mo₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇ + K₂O) system was conducted in the present study and previously ¹⁴⁻¹⁶, and optimized model parameters were obtained. Since the reactions 2 A₂MO₄ = A₂M₂O₇ + A₂O (where A = Na, K and M = Cr, Mo) are very limited up to above the liquidus temperatures, ¹⁷ the free oxides were present in the liquid phase in dilute amounts. The present paper describes all molybdate-based and dimolybdate-based sub-systems for which experimental data (mainly phase equilibria) were available. Due to the lack of data, DSC-TGA experiments were performed at several compositions in the common-ion sub-systems (Na₂CO₃ + Na₂MoO₄), (Na₂SO₄ + Na₂MoO₄), (K₂SO₄ + K₂MoO₄), (Na₂CrO₄ + Na₂MoO₄), (K₂CrO₄ + K₂MoO₄), and (Na₂MoO₄ + K₂MoO₄).

No solid solubility was introduced at low temperatures in $(Na_2CO_3 + Na_2MoO_4)$ since our DSC thermal arrests were consistent with solid-solid transitions for the Na₂CO₃ and Na₂MoO₄ pure compounds. In $(Na_2SO_4 + Na_2MoO_4)$, overall our DSC results for Na₂MoO₄-rich compositions agreed with the experimental data from the literature. Owing to the same crystal structure and space group of Na₂SO₄(S1) and Na₂CrO₄(S1), the $(Na_2SO_4 + Na_2MoO_4)$ and $(Na_2CrO_4 + Na_2MoO_4)$ phase diagrams were modeled simultaneously; two Na₂MoO₄-rich solid solutions $(Na_2MoO_4(S2)$ -ss-rich and cF56) were introduced at intermediate temperatures. In $(Na_2MoO_4 + K_2MoO_4)$, particular attention was paid to the

molybdenum-glaserite phase (hP14). Mechanical mixtures of the pre-treated reagents and an equilibrated sample (to which an excess of Na_2MoO_4 or K_2MoO_4 was added subsequently) were both studied to best characterize the compositional range of hP14 and its phase boundaries.

The Modified Quasichemical Model in the Quadruplet Approximation (MQMQA) was used to model the liquid solution and the high-temperature hexagonal solid solution hP22, while the Compound Energy Formalism (CEF) was used for all other solid solutions. All experimental data from the literature and from this study were reproduced within experimental error limits.

Using the model parameters obtained for the binary, ternary common-cation and ternary reciprocal sub-systems along with suitable interpolation methods, it is possible, from the MQMQA, to predict accurately the thermodynamic properties of the multicomponent liquid. The developed thermodynamic model is compatible with the FactSage software package ¹⁸ and can be used to calculate phase equilibria in the multicomponent system, thus permitting the investigation of high-temperature corrosion, in particular between 600 and 950° C.

Acknowledgements

Ms. Sara Benalia would like to thank the Canada Research Chair in Computational Thermodynamics for High Temperature Sustainable Processes held by Prof. Patrice Chartrand, and the Johan Gadolin Process Chemistry Centre for the 5 month-mobility grant awarded for her stay at Åbo Akademi University (Turku, Finland). The authors would like to thank Mr. Peter Backman and Ms. Jaana Paananen for operating the DSC apparatuses, and Ms. Evguenia Sokolenko for helping locate old articles and for translating them into English.

Supporting information

DSC-TGA measurements for molybdate-based common-ion binary sub-systems, SEM secondary electron images of equilibrated molybdenum-glaserite, and additional calculated isoplethal sections in the (Na₂SO₄ + Na₂CrO₄ + Na₂MoO₄) and (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) systems. This information is available free of charge via the Internet at <u>http://pubs.acs.org/</u>.

References

(1) Eliaz, N.; Shemesh, G.; Latanision, R. Hot corrosion in gas turbine components. *Eng. Fail. Anal.* **2002**, *9*, 31-43.

(2) Stringer, J. High-temperature corrosion of superalloys. *Corros. Sci. Technol.* **1987**, *3*, 482-493.

(3) Nicholls, J. R. Designing oxidation-resistant coatings. *JOM* **2000**, *52*, 28-35. DOI: 10.1007/s11837-000-0112-2.

(4) Benalia, S.; Tesfaye, F.; Lindberg, D.; Sibarani, D.; Hupa, L.; Chartrand, P.; Robelin, C. Critical Evaluation and Calorimetric Study of the Thermodynamic Properties of Na₂CrO₄, K₂CrO₄, Na₂MoO₄, K₂MoO₄, Na₂WO₄, and K₂WO₄. *Revision submitted for publication in J. Phys. Chem. Ref. Data.* **2023**.

(5) Stringer, J. Hot Corrosion of High-Temperature Alloys. *Annu. Rev. Mater. Sci.* **1977**, 7, 477-509. DOI: 10.1146/annurev.ms.07.080177.002401.

(6) Baxter, L. L.; Miles, T. R.; Miles, T. R.; Jenkins, B. M.; Milne, T.; Dayton, D.; Bryers, R. W.; Oden, L. L. The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. *Fuel Process. Technol.* **1998**, *54*, 47-78. DOI: https://doi.org/10.1016/S0378-3820(97)00060-X.

(7) Nielsen, H. P.; Frandsen, F. J.; Dam-Johansen, K.; Baxter, L. L. The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. *Prog. Energy Combust. Sci.* 2000, *26*, 283-298. DOI: https://doi.org/10.1016/S0360-1285(00)00003-4.
(8) Paneru, M.; Stein-Brzozowska, G.; Maier, J. r.; Scheffknecht, G. n. Corrosion mechanism of alloy 310 austenitic steel beneath NaCl deposit under varying SO₂ concentrations in an oxy-fuel combustion atmosphere. *En. Fuels.* 2013, *27*, 5699-5705.
(9) Lehmusto, J.; Lindberg, D.; Yrjas, P.; Skrifvars, B.-J.; Hupa, M. Studies on the partial reactions between potassium chloride and metallic chromium concerning corrosion at elevated temperatures. *Oxid. Met.* 2012, *77*, 129-148.

(10) Fryburg, G.; Kohl, F.; Stearns, C. Chemical Reactions Involved in the Initiation of Hot Corrosion of IN-738. *J. Electrochem. Soc.* **1984**, *131*, 2985-2997.

(11) Fryburg, G. C.; Kohl, F. J.; Stearns, C. A.; Fielder, W. L. Chemical Reactions Involved in the Initiation of Hot Corrosion of B-1900 and NASA-TRW VIA. *J. Electrochem. Soc.* **1982**, *129*, 571-585. DOI: 10.1149/1.2123928. (12) Misra, A. K. Mechanism of Na₂SO₄-Induced Corrosion of Molybdenum Containing Nickel-Base Superalloys at High Temperatures I. Corrosion in Atmospheres Containing Only. *J. Electrochem. Soc.* **1986**, *133*, 1029-1038.

(13) Peters, K.; Whittle, D.; Stringer, J. Oxidation and hot corrosion of nickel-based alloys containing molybdenum. *Corros. Sci.* **1976**, *16*, 791-804.

(14) Lindberg, D.; Backman, R.; Chartrand, P. Thermodynamic evaluation and optimization of the (Na₂SO₄+ K₂SO₄+ Na₂S₂O₇+ K₂S₂O₇) system. *J. Chem. Thermodyn.* **2006**, *38*, 1568-1583.

(15) Lindberg, D.; Backman, R.; Chartrand, P. Thermodynamic evaluation and optimization of the (NaCl+ Na₂SO₄+ Na₂CO₃+ KCl+ K₂SO₄+ K₂CO₃) system. *J. Chem. Thermodyn.* **2007**, *39*, 1001-1021.

(16) Benalia, S.; Tesfaye, F.; Lindberg, D.; Hupa, L.; Chartrand, P.; Robelin, C. Thermodynamic Evaluation and Optimization of the (NaCl+Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂O+KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇

+K₂CrO₄+K₂Cr₂O₇ + K₂O) System Involved in High Temperature Corrosion. *Submitted for publication in J. Therm. Anal. Calorim.* **2023**.

(17) Benalia, S.; Chartrand, P.; Robelin, C. Critical Evaluation of the Thermodynamic Properties of Na₂Cr₂O₇, K₂Cr₂O₇, Na₂Mo₂O₇, K₂Mo₂O₇, Na₂W₂O₇, and K₂W₂O₇. *Revision submitted for publication in J. Phys. Chem. Ref. Data.* **2023**.

(18) Bale, C. W.; Bélisle, E.; Chartrand, P.; Decterov, S. A.; Eriksson, G.; Gheribi, A. E.; Hack, K.; Jung, I. H.; Kang, Y. B.; Melançon, J.; et al. FactSage thermochemical software and databases, 2010–2016. *Calphad* **2016**, *54*, 35-53. DOI: https://doi.org/10.1016/j.calphad.2016.05.002.

(19) Pelton, A. D.; Chartrand, P. Thermodynamic evaluation and optimization of the LiCl-NaCl-KCl-RbCl-CsCl-MgCl₂-CaCl₂ system using the modified quasi-chemical model. *Metall. Mater. Trans. A* 2001, *32*, 1361-1383. DOI: 10.1007/s11661-001-0227-2.
(20) Lindberg, D.; Backman, R.; Chartrand, P. Thermodynamic evaluation and optimization of the (Na₂CO₃+ Na₂SO₄+ Na₂S+ K₂CO₃+ K₂SO₄+ K₂S) system. *J. Chem. Thermodyn.* 2007, *39*, 942-960.

(21) γ-Na₂CO₃ (Na2[CO3] rt) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd_2042290); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_2042290 (accessed. (22) Hall, S. R.; McMahon, B. *International tables for crystallography, definition and exchange of crystallographic data*; Springer: Dordrecht, **2005**, 8, 1-904.

(23) Na₂S₂O₇ (Na2[S2O7]) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd_1838862); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_1838862 (accessed. (24) Na₂CrO₄ (Na₂[CrO₄] rt) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd 1001365); Springer-Verlag

Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_1001365 (accessed. (25) β-Na₂Cr₂O₇ (Na₂[Cr₂O₇] rt) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd_1401687); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_1401687 (accessed. (26) α-Na₂Cr₂O₇ (Na2[Cr2O7] ht) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd_1100126); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_1100126 (accessed. (27) K₂CrO₄ (K2[CrO4] tar) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd_0377606); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_0377606 (accessed. (28) K₂Cr₂O₇ (K2[Cr2O7] rt) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd_1322711); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_1322711 (accessed. (29) Na₂MoO₄ (Na2[MoO4] rt) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd_1815021); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_1815021 (accessed.

(30) Na₂Mo₂O₇ rt structural transitions: Datasheet from "PAULING FILE Multinaries

Edition – 2022" in SpringerMaterials (https://materials.springer.com/isp/physicalproperty/docs/ppp_2e7a378246c34f711dc6882c95f111c4); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for

Materials Science (NIMS), Japan: https://materials.springer.com/isp/physical-property/docs/ppp 2e7a378246c34f711dc6882c95f111c4 (accessed.

(31) K_2MoO_4 ($K_2[MoO_4]$ rt) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials

(https://materials.springer.com/isp/crystallographic/docs/sd_1220174); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_1220174 (accessed.

(32) *K*₂*Mo*₂*O*₇ *Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials*

(https://materials.springer.com/isp/crystallographic/docs/sd_1610363); Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan:

https://materials.springer.com/isp/crystallographic/docs/sd_1610363 (accessed.
(33) Pelton, A. D.; Chartrand, P.; Eriksson, G. The modified quasi-chemical model: Part IV. Two-sublattice quadruplet approximation. *Metall. Mater. Trans. A* 2001, *32*, 1409-1416.

(34) Pelton, A. D.; Chartrand, P. The modified quasi-chemical model: Part II. Multicomponent solutions. *Metall. Mater. Trans. A* **2001**, *32*, 1355-1360.

(35) Lambotte, G.; Chartrand, P. Thermodynamic optimization of the (Na₂O + SiO₂ +

NaF + SiF₄) reciprocal system using the Modified Quasichemical Model in the Quadruplet Approximation. *J. Chem. Thermodyn.* **2011**, *43*, 1678-1699. DOI: 10.1016/j.jct.2011.05.038.

(36) Sundman, B.; Ågren, J. A regular solution model for phases with several components and sublattices, suitable for computer applications. *J. Phys. Chem. Solids* **1981**, *42*, 297-301.

(37) Hillert, M.; Jansson, B.; Sundman, B. Application of the Compound-Energy Model to Oxide Systems. *J. Mater. Res.* **1988**, *79*, 81-87. DOI: doi:10.1515/ijmr-1988-790203.
(38) Hillert, M. The compound energy formalism. *J. Alloys Compd.* **2001**, *320*, 161-176. DOI: https://doi.org/10.1016/S0925-8388(00)01481-X.

(39) Jin, L.; Lindberg, D.; Tsuchiyama, Y.; Robelin, C. A thermodynamic model for high temperature corrosion applications: The $(Na_2SO_4 + K_2SO_4 + ZnSO_4 + PbSO_4)$ system. *Chem. Eng. Sci.* **2022**, *260*, 117847. DOI: https://doi.org/10.1016/j.ces.2022.117847. (40) Fábry, J.; Petricek, V.; Vanek, P.; Cisarova, I. Phase transition in K₃Na(MoO₄)₂ and determination of the twinned structures of K₃Na(MoO₄)₂ and K_{2.5}Na_{1.5}(MoO₄)₂ at room temperature. *Acta Cryst. B.* **1997**, *53*, 596-603.

(41) Temkin, M. Mixtures of fused salts as ionic solutions. *Acta Physicochim. URSS* **1945**, *20*, 411.

(42) Sangster, J. M.; Pelton, A. D. Phase diagrams and thermodynamic properties of the 70 binary alkali halide systems having common ions. *J. Phys. Chem. Ref. Data.* **1987**, *16*, 509-561.

(43) Rycerz, L. Practical remarks concerning phase diagrams determination on the basis of differential scanning calorimetry measurements. *J. Therm. Anal. Calorim.* **2013**, *113*, 231-238. DOI: 10.1007/s10973-013-3097-0.

(44) Bukhalova, G. A.; Mateiko, Z. A. Complex formation and solid solutions in the adiagonal reciprocal system of the molybdates and chlorides of sodium and potassium. *Zh. Obshch. Khim.* **1955**, *25*, 851-857.

(45) Shurdumov, G. K.; Khakulov, Z. L.; Mokhosoev, M. V.; Kodzokov, K. A.; El'mesova, R. M. Thermal analysis, density, and molar volumes of melts of binary systems of sodium and potassium molybdates, tungstates, and carbonates. *Zh. Neorg. Khim.* **1984**, *29*, 2096-2101.

(46) Boeke, H. E. Die Mischkristalle von wasserfreiem Natrium-Sulfat,-Molybdat und - Wolframat. Z. Anorg. Allg. Chem. **1906**, *50*, 355.

(47) Belyaev, I. N.; Doroshenko, A. K. Exchange decomposition in the reciprocal system of sodium and silver sulfate and molybdate. *Zh. Obshch. Khim.* 1954, *24*, 427-432.
(48) Mateiko, Z. A.; Bukhalova, G. A. Solid solutions in the systems: (1) Na||SO4, CrO4, MoO4; (2) Na||SO4, CrO4, WO4; (3) Na||SO4, MoO4, WO4; (4) Na||CrO4, MoO4, WO4. *Zh. Neorg. Khim.* 1959, *4*, 2329-2334.

(49) Simoes, M. C.; Hughes, K. J.; Ingham, D. B.; Ma, L.; Pourkashanian, M. Estimation of the Thermochemical Radii and Ionic Volumes of Complex Ions. *Inorg. Chem.* **2017**, *56*, 7566-7573. DOI: 10.1021/acs.inorgchem.7b01205.

(50) Amadori, M. The Neutral Behavior of Alkaline Sulfates, Chromates, Molybdates and Tungstates at Low and High Temperatures. II. *Atti Accad. Lincei, Rend. Sci. Fis. Mat. Nat.* **1913**, *22*, 453-459.

(51) Bergman, A. G.; Kislova, A. I.; Korobka, E. I. The ternary adiagonal-belt type reciprocal system of sulfates and molybdates of lithium and potassium. *Zh. Neorg. Khim.* **1954**, *24*, 1127-1135.

(52) Mateiko, Z. A.; Bukhalova, G. A. Quaternary system K₂SO₄-K₂CrO₄-K₂MoO₄-K₂WO₄. *Zh. Neorg. Khim.* **1960**, *5*, 2071-2075.

(53) Belyaev, I. N.; Sholokhovich, M. L. Complex formation and exchange decomposition in the reciprocal system of the pyrophosphates and molybdates of sodium and potassium. *Zh. Obshch. Khim.* **1953**, *23*, 1265-1273.

(54) Amadori, M. Sulle capacità dei sali sodici e potassici di dare composti e cristalli misti. *Atti Accad. Lincei, Rend. Sci. Fis. Mat. Nat.* **1913**, *72*, 903-932.

(55) Ding, Y.; Hou, N.; Chen, N.; Xia, Y. Phase diagrams of Li₂MoO₄-Na₂MoO₄ and Na₂MoO₄-K₂MoO₄ systems. *Rare Met.* **2006**, *25*, 316-320. DOI:

https://doi.org/10.1016/S1001-0521(06)60060-0.

(56) Eysel, W. CRYSTAL-CHEMISTRY OF SYSTEM Na₂SO₄-K₂SO₄-K₂CrO₄-Na₂CrO₄ AND OF GLASERITE PHASE. *Am. Mineral.* **1973**, *58*, 736-747.

(57) Chartrand, P.; Pelton, A. D. A predictive thermodynamic model for the Al-NaF-AlF₃-CaF₂-Al₂O₃ system. *Light Met. (Warrendale, PA, U. S.)* **2002**, 245-252.

(58) Saal, J. E.; Kirklin, S.; Aykol, M.; Meredig, B.; Wolverton, C. Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Materials Database (OQMD). *TMS.* **2013**, *65*, 1501-1509. DOI: 10.1007/s11837-013-0755-4.

(59) Kirklin, S.; Saal, J. E.; Meredig, B.; Thompson, A.; Doak, J. W.; Aykol, M.; Rühl, S.; Wolverton, C. The Open Quantum Materials Database (OQMD): assessing the accuracy of DFT formation energies. *npj Comput. Mater.* **2015**, *1*, 15010. DOI: 10.1038/npjcompumats.2015.10.

(60) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; et al. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater.* **2013**, *1*, 011002. DOI: 10.1063/1.4812323.

(61) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst. A.* **1976**, *32*, 751-767.

(62) Amadori, M. The Relative Behavior of Alkali Sulfates, Chromates, Molybdates and Tungstates at High and Low Temperatures. III. *Atti Accad. Lincei, Rend. Sci. Fis. Mat. Nat.* **1913**, *22*, 609-616.

(63) Groschuff, E. Über Wasserfreie Molybdate I. Z. Anorg. Allg. Chem. **1908**, 58, 113-119. DOI: https://doi.org/10.1002/zaac.19080580112.

(64) Hoermann, F. Molybdates and tungstates. Binary systems: Li₂MoO₄-MoO₃,

Na2MoO4-MoO3, K2MoO4-MoO3, Li2WO4-WO3, Na2WO4-WO3, K2WO4-WO3,

Li₂MoO₄-Na₂MoO₄, Li₂WO₄-Na₂WO₄, Li₂MoO₄-K₂MoO₄. Z. Anorg. Allg. Chem. **1928**, 177, 145-186, 10.1002/zaac.19291770117. DOI: 10.1002/zaac.19291770117.

(65) Caillet, P. Anhydrous sodium or potassium polymolybdates and polytungstates. *Bull. Soc. Chim. Fr.* **1967**, (12), 4750-4755.

(66) Fedorov, P. I.; Mokhosoev, M. V. Reaction of sodium carbonate with disodium ditungstate and dimolybdate. *Zh. Neorg. Khim.* **1961**, *6*, 123-124.

(67) Amadori, M. Analisi termica dei polimolibdati e poliwolframati di potassio. *Atti Accad. Lincei, Rend. Sci. Fis. Mat. Nat.* **1913**, *72*, 893-902.

TOC Graphic (For table of contents only)

