

Titre: Modèle thermodynamique pour les chromates, molybdates et tungstates de sodium et de potassium impliqués dans la corrosion des aciers à haute température
Title:

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Author:

Date: 2023

Type: Mémoire ou thèse / Dissertation or Thesis

Référence: Benalia, S. (2023). Modèle thermodynamique pour les chromates, molybdates et tungstates de sodium et de potassium impliqués dans la corrosion des aciers à haute température [Thèse de doctorat, Polytechnique Montréal]. PolyPublie.
Citation: <https://publications.polymtl.ca/54781/>

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URL de PolyPublie: <https://publications.polymtl.ca/54781/>
PolyPublie URL:

Directeurs de recherche: Patrice Chartrand, & Christian Robelin
Advisors:

Programme: Génie métallurgique
Program:

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Modèle thermodynamique pour les chromates, molybdates et tungstates de sodium et de potassium impliqués dans la corrosion des aciers à haute température

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Département de génie chimique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*

Génie métallurgique

Août 2023

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Cette thèse intitulée :

Modèle thermodynamique pour les chromates, molybdates et tungstates de sodium et de potassium impliqués dans la corrosion des aciers à haute température

présentée par **Sara BENALIA**

en vue de l'obtention du diplôme de *Philosophiæ Doctor*

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DÉDICACE

À ma famille

REMERCIEMENTS

Tout d'abord, je tiens à remercier mon directeur de recherche, Patrice Chartrand, pour m'avoir donnée l'opportunité de travailler sur ce projet, en particulier la possibilité de réaliser en partie ce travail à l'étranger. Ses recommandations et commentaires pertinents ont considérablement contribué à la qualité scientifique du présent travail.

Je tiens particulièrement à remercier Christian Robelin pour son excellent encadrement et son approche rigoureuse pendant les cinq dernières années. Sa contribution a grandement contribué à la réussite de ce projet.

Merci à Leena Hupa de m'avoir accueillie pendant huit mois au sein du laboratoire de science et d'ingénierie moléculaires de l'Université Åbo Akademi (Finlande).

Merci à Peter Backman pour son assistance et ses précieux conseils lors de mon apprentissage de la technique expérimentale (DSC-TGA).

Un immense merci à Fiseha Tesfaye et Daniel Lindberg pour leur engagement dans ce projet. Leur contribution a été d'une importance capitale pour mener à bien les mesures expérimentales.

Merci à Evguenia Sokolenko pour l'aide qu'elle m'a apportée dans la recherche d'anciens articles et leur traduction en anglais. Je tiens également à remercier Aïmen E. Gheribi de m'avoir expliquée certains aspects mathématiques de la DFT.

Je dois une profonde gratitude à mes parents, mon mari, mes sœurs, mes beaux-parents et tous mes collègues du CRCT pour leur soutien et leurs encouragements inconditionnels tout au long de ma thèse de doctorat. Leur appui a été essentiel et sans eux, cette réalisation n'aurait pas été possible.

RÉSUMÉ

L'objectif principal de cette étude est de mieux comprendre les réactions chimiques de corrosion à haute température (entre 600 et 950°C), connue sous le nom de « corrosion chaude », lors des procédés de conversion de l'énergie par combustion dans des milieux riches en O-H-S-C-Cl et en sels alcalins. Pour ce faire, nous avons analysé de nombreuses réactions chimiques susceptibles de se produire puis développé un nouveau modèle thermodynamique multicomposant permettant de prédire les phases corrosives susceptibles de se former dans ces environnements.

Les installations en acier et en acier inoxydable contenant les éléments d'alliage Ni, Cr, Mo, W et V peuvent être sujettes à ce type de corrosion. Typiquement entre 600 et 950°C, des gaz corrosifs (CO_2 , SO_2 , O_2 , H_2O , etc.), des cendres volantes (NaCl , KCl , Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3 , etc.), des dépôts solides, voire des sels fondus, peuvent se former. Les sels fondus pouvant se former sont (NaCl , KCl , Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3 , $\text{Na}_2\text{S}_2\text{O}_7$, et $\text{K}_2\text{S}_2\text{O}_7$), (Na_2CrO_4 et K_2CrO_4), (Na_2MoO_4 et K_2MoO_4), (Na_2WO_4 et K_2WO_4), et ($\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{W}_2\text{O}_7$, et $\text{K}_2\text{W}_2\text{O}_7$). Ils déclenchent une série de réactions ayant un impact néfaste sur la durabilité et la performance des équipements utilisés.

Les phases solides et liquide faisant intervenir ces sels alcalins sont prises en compte dans le nouveau modèle thermodynamique développé pour le système ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) (dilué en Na_2O et en K_2O). Ce modèle permet d'évaluer les conditions limites pouvant favoriser la formation de dépôts de chromates, dichromates, molybdates, et dimolybdates de sodium et de potassium, et d'éventuellement prévenir la formation de ces dépôts.

Dans un premier temps, nous avons évalué les données cristallographiques et les propriétés thermodynamiques ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$ et C_P) des composés A_2MO_4 et $\text{A}_2\text{M}_2\text{O}_7$ (où $\text{A} = \text{Na}$ ou K , et $\text{M} = \text{Cr}$, Mo ou W). En particulier, nous avons pu identifier plus aisément les solutions solides susceptibles de se former. Lors de l'estimation des propriétés thermodynamiques des douze

composés purs, les données expérimentales les plus fiables issues de la littérature et nos mesures de DSC-TGA pour les six sels purs A_2MO_4 ont été utilisées.

Par la suite, nous avons ajouté au modèle thermodynamique existant pour le système ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7$) les chromates et dichromates de sodium et de potassium, puis les molybdates et dimolybdates de sodium et de potassium. Nous avons adopté la méthode CALPHAD (CALculation of PHase Diagrams). Le modèle développé est compatible avec le logiciel thermochimique FactSage. La phase liquide et la solution solide hexagonale hP22 de haute température ($Na_2CO_3 + Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4 + K_2CO_3 + K_2SO_4 + K_2CrO_4 + [K_2MoO_4]$) ont été modélisées avec le Modèle Quasichimique Modifié dans l'Approximation des Quadruplets (MQMQA), tandis que le « Compound Energy Formalism » (CEF) a été utilisé pour toutes les autres solutions solides. Ainsi, 23 sous-systèmes binaires à ion commun ont été modélisés, et les paramètres de modèles correspondants ont été obtenus. Les données d'équilibres de phases les plus fiables issues de la littérature ainsi que les données générées par nos 56 expériences de DSC-TGA ont été prises en compte.

Des analyses de EDS-SEM et de DSC-TGA ont été effectuées pour les phases non-stœchiométriques de glasérite de chrome $K_3Na(CrO_4)_2$ et de glasérite de molybdène $K_3Na(MoO_4)_2$ afin de mesurer la gamme de compositions de la solution solide hP14 dans les sous-systèmes binaires à anion commun ($Na_2CrO_4 + K_2CrO_4$) et ($Na_2MoO_4 + K_2MoO_4$), respectivement.

Il est possible de prédire de manière fiable les propriétés thermodynamiques de la phase liquide multicomposante à l'aide du MQMQA, en utilisant les paramètres de modèles optimisés pour les sous-systèmes binaires à ion commun, ternaires à cation commun (Na^+ ou K^+), et ternaires réciproques (avec Na^+ , K^+ , et deux anions). De plus, plusieurs solutions solides multicomposantes (hP22, oS28, oP28, hP14, oF56, cF56, $K_2MoO_4(s_3)$ -ht-ss, $Na_2MoO_4(s_2)$ -ss-rich, $K_2Cr_2O_7(s.s)$, aP44 et aP22) ont été modélisées dans le cadre de cette étude.

Le modèle thermodynamique développé dans ce travail permet de faire des calculs thermodynamiques et d'équilibres de phases pouvant servir à développer des stratégies de prévention et de protection efficaces destinées à minimiser les effets néfastes de la corrosion chaude.

ABSTRACT

The main objective of this study is to better understand high-temperature corrosion chemical reactions (between 600 and 950°C), known as « hot corrosion », during energy conversion processes through combustion in environments rich in O-H-S-C-Cl and alkaline salts. We analyzed numerous chemical reactions that might occur and then developed a new multicomponent thermodynamic model permitting to predict the corrosive phases that may form in these environments.

Steel and stainless steel installations consisting of the alloying elements Ni, Cr, Mo, W and V can be subject to this type of corrosion. Typically, between 600 and 950°C, corrosive gases (CO₂, SO₂, O₂, H₂O, etc.), fly ashes (NaCl, KCl, Na₂SO₄, K₂SO₄, Na₂CO₃, K₂CO₃, etc.), solid deposits and even molten salts may form. The molten salts that can form are (NaCl, KCl, Na₂SO₄, K₂SO₄, Na₂CO₃, K₂CO₃, Na₂S₂O₇, and K₂S₂O₇), (Na₂CrO₄ and K₂CrO₄), (Na₂MoO₄ and K₂MoO₄), (Na₂WO₄ and K₂WO₄), and (Na₂Cr₂O₇, K₂Cr₂O₇, Na₂Mo₂O₇, K₂Mo₂O₇, Na₂W₂O₇, and K₂W₂O₇). They can trigger a series of reactions having a detrimental impact on the durability and performance of the equipments used.

The solid and liquid phases involving these alkaline salts are considered in the new thermodynamic model developed for the system (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂MoO₄ + Na₂Mo₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇ + K₂O) (diluted in Na₂O and K₂O). The model permits to assess the limiting conditions that could favor the formation of deposits of chromates, dichromates, molybdates, and dimolybdates of sodium and potassium, and possibly prevent the formation of these deposits.

As a first step, we assessed the crystallographic data and thermodynamic properties ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$ and C_P) of the A₂MO₄ and A₂M₂O₇ compounds (where A = Na or K, and M = Cr, Mo or W). In particular, we identified more easily the solid solutions that may form. During the assessment of the thermodynamic properties of the twelve pure compounds, the most reliable experimental data from the literature and our DSC-TGA measurements for the six pure salts

A_2MO_4 were used.

As a second step, we added to the existing thermodynamic model for the system ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7$) the chromates and dichromates of sodium and potassium, and then the molybdates and dimolybdates of sodium and potassium. The CALPHAD (CALculation of PHase Diagrams) method was adopted. The developed model is compatible with the FactSage thermochemical software. The liquid phase and the high-temperature hP22 hexagonal solid solution ($Na_2CO_3 + Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4 + K_2CO_3 + K_2SO_4 + K_2CrO_4 + [K_2MoO_4]$) were modeled with the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA), whereas the Compound Energy Formalism (CEF) was used for all other solid solutions. Thus, 23 common-ion binary sub-systems were modeled, and the corresponding model parameters were obtained. The most reliable phase equilibrium data from the literature and the data generated by our 56 DSC-TGA experiments were taken into account.

EDS-SEM and DSC-TGA analyses were conducted for the non-stoichiometric phases of chrome-glaserite $K_3Na(CrO_4)_2$ and molybdenum-glaserite $K_3Na(MoO_4)_2$ to measure the composition range of the hP14 solid solution in the common-anion binary sub-systems ($Na_2CrO_4 + K_2CrO_4$) and ($Na_2MoO_4 + K_2MoO_4$), respectively.

It is possible to predict reliably the thermodynamic properties of the multicomponent liquid phase with the MQMQA, using the optimized model parameters for the binary common-ion, ternary common-cation (Na^+ or K^+), and ternary reciprocal (with Na^+ , K^+ , and two anions) sub-systems. Moreover, several multicomponent solid solutions (hP22, oS28, oP28, hP14, oF56, cF56, $K_2MoO_4(s_3)$ -ht-ss, $Na_2MoO_4(s_2)$ -ss-rich, $K_2Cr_2O_7(s.s)$, aP44 and aP22) were modeled in this study.

The thermodynamic model developed in this work permits to perform thermodynamic and phase equilibrium calculations that could serve to develop effective prevention and protection strategies, in order to minimize the detrimental effects of hot corrosion.

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LISTE DES SIGLES ET ABRÉVIATIONS

CALPHAD	<i>CAL</i> culat <i>ion of PHA</i> se <i>Diagrams</i>
CEF	<i>Compound Energy Formalism</i>
C_p	Capacité calorifique à pression constante
DFT	<i>Density Functional Theory</i>
DRX (XRD)	Diffraction des Rayons X (<i>X-Ray Diffraction</i>)
DSC	Calorimétrie différentielle à balayage (<i>Differential Scanning Calorimetry</i>)
DTA	Analyse thermique différentielle (<i>Differential Thermal Analysis</i>)
EDS	Spectroscopie de rayons X à dispersion d'énergie (<i>Energy Dispersive X-ray Spectroscopy</i>)
ΔG°	Énergie de Gibbs
$\Delta H_{298.15\text{ K}}^\circ$	Enthalpie standard de formation
MEB (SEM)	Microscopie Électronique à Balayage (<i>Scanning Electron Microscopy</i>)
MQMQA	Modèle Quasichimique Modifié dans l'Approximation des Quadruplets (<i>Modified Quasichemical Model in the Quadruplet Approximation</i>)
NIST-JANAF	<i>National Institute of Standards and Technology — Joint Army-Navy-Air Force</i>
OQMD	<i>Open Quantum Materials Database</i>
$p(\text{O}_2)$	Pression partielle de l'oxygène
$S_{298.15\text{ K}}^\circ$	Entropie absolue
T	Température
TGA	Thermogravimétrie
Indices	
config	Configurationnel(le)
f	Fusion
max	Maximal(e)
trans	Transition

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CHAPITRE 1 INTRODUCTION

La portée de cette recherche s'inscrit dans le thème générique de la modélisation des réactions chimiques de corrosion dans les procédés de haute température, lors des phénomènes de conversion d'énergie, d'écaillage et de corrosion, pour des systèmes convertissant principalement de la matière organique en énergie.

Ce projet de recherche est pertinent pour la modélisation et la compréhension de phénomènes de corrosion rencontrés dans plusieurs applications telles que le procédé de fabrication de papiers Kraft [1, 2], les incinérateurs de déchets ménagers (procédé de pyrolyse ou de gazéification, etc.) [3, 4], les centrales à combustibles fossiles [5-7], combustibles organiques (charbon, pétrole et gaz naturel, etc.) [8, 9] ou encore biocombustibles issus de la biomasse [10-13], les turbines à gaz des moteurs d'avions ou de bateaux [14-17] ainsi que les réacteurs chimiques à haute température utilisés dans l'industrie pétrochimique [18].

Les installations de traitement thermique sont essentiellement fabriquées à partir d'aciers et d'aciers inoxydables contenant des éléments d'alliage tels que Ni, Cr, Mo, W et V [19-23]. Dans les conditions de mise en service, les gaz de combustion (N_2 , CO_2 , CO, O_2 , H_2O , etc) contenant des impuretés (SO_2 , Cl_2 , S_2 , HCl, etc.), et la présence d'éléments tels que K, Na, Ca, Mg, Fe, Al, Si, P, S, Cl, C, H et O [24, 25] favorisent la formation de gaz corrosifs (CO_2 , SO_2 , O_2 , H_2O , etc) et de cendres volantes (NaCl, KCl, Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3 , etc.) [14, 20, 26, 27]. Ainsi, des dépôts solides voire des sels fondus peuvent se former et entraîner une corrosion potentiellement sévère, particulièrement si une phase liquide devient stable, augmentant les vitesses de corrosion.

Ce phénomène est connu sous le nom de corrosion chaude (« hot corrosion ») et est généré par des sels fondus corrosifs tels que ((NaCl, KCl, Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3 , $Na_2S_2O_7$, et $K_2S_2O_7$ [28]), (Na_2CrO_4 et K_2CrO_4 [29-31]), (Na_2MoO_4 [30-32] et K_2MoO_4 [31]), (Na_2WO_4 [30, 31, 33] et K_2WO_4 [31]), et ($Na_2Cr_2O_7$, $K_2Cr_2O_7$, $Na_2Mo_2O_7$, $K_2Mo_2O_7$, $Na_2W_2O_7$, et $K_2W_2O_7$ [34])). Ces sels fondus sont formés suite à l'action combinée des cendres volantes, des gaz corrosifs et d'autres produits de corrosion (Na_2O , K_2O , NaOH, KOH, etc.) [20, 26, 35].

Les dépôts de sels, en se liquéfiant, accentuent le risque de corrosion car ils peuvent dissoudre partiellement les couches d'oxyde protectrices (i.e. dites passivantes) et donc attaquer la surface du métal. En effet, les cendres et sels déposés sur les parois métalliques modifient le potentiel chimique de l'environnement à l'interface avec le métal, et contribuent à cette détérioration. En présence d'oxygène et de soufre, le dépôt de sels diminue le potentiel d'oxygène et augmente celui du soufre, entravant ainsi la formation d'une couche d'oxyde protectrice durable [36].

Un exemple typique est la combustion de la liqueur noire issue de la fabrication du papier kraft, qui a lieu dans la chaudière de récupération des usines de pâtes et papiers grâce à l'air injecté à plusieurs étages. Des gaz de combustion (CO_2 , SO_2 , H_2O , etc.) et de la chaleur sont générés. Cette chaleur est échangée avec de l'eau circulant dans des échangeurs, permettant ainsi la production d'électricité utilisée par les usines. Pour avoir un bon rendement thermodynamique, le combustible est brûlé avec un excès d'oxygène de 5 à 10%, générant ainsi plus de chaleur.

Dans certaines conditions, il peut se former des sels fondus très corrosifs, entraînant une transformation partielle de la couche d'oxyde protectrice de l'acier en chromates, molybdates, tungstates et/ou vanadates. On parle alors de corrosion "catastrophique". En général, les échangeurs de chaleur sont opérés à des températures voisines de 500°C , un peu en dessous de la température de corrosion "catastrophique".

Plusieurs optimisations thermodynamiques de systèmes chimiques pertinents pour la corrosion ont été faites antérieurement. En particulier, Liang et al [37, 38] ont effectué une évaluation et optimisation thermodynamique du système ($\text{NaCl} + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{WO}_4$). Par la suite, Lindberg et al [28] ont mené une analyse chimique détaillée des dépôts solides formés sur les échangeurs de chaleur. Cette analyse a révélé la présence majoritaire de KCl , K_2CO_3 et K_2SO_4 ainsi que de faibles quantités de NaCl , Na_2CO_3 et Na_2SO_4 [28]. Un modèle thermodynamique fiable a été développé par Lindberg et al [39-41] pour le système ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7$). Ce modèle a, en particulier, une grande importance pour la combustion de la liqueur noire dans les chaudières de récupération des usines de pâtes et papiers. Il permet de faire des calculs thermodynamiques complexes à l'aide du logiciel thermochimique FactSage [42].

Dans le cadre de cette étude, une attention particulière a été accordée aux produits de corrosion liés aux éléments d'alliage Cr, Mo et W. En raison de la présence d'un excès d'oxygène dans les gaz de combustion, les oxydes de ces éléments, tels que Cr_2O_3 [21, 29], MoO_3 et WO_3 [21, 23, 36], peuvent réagir pour former des chromates et dichromates (Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$ et $\text{K}_2\text{Cr}_2\text{O}_7$) sous forme solide ou liquide. De même, des molybdates et dimolybdates (Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$ et $\text{K}_2\text{Mo}_2\text{O}_7$) ainsi que des tungstates et ditungstates (Na_2WO_4 , K_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$ et $\text{K}_2\text{W}_2\text{O}_7$) peuvent se former.

Afin d'améliorer notre compréhension des phénomènes de corrosion et de prévenir particulièrement la formation de produits corrosifs liquides, ces différents composés chimiques ont été intégrés au modèle thermodynamique existant [39-41]. Notre objectif initial était de développer un modèle thermodynamique pour le système complet ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{WO}_4 + \text{Na}_2\text{W}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{WO}_4 + \text{K}_2\text{W}_2\text{O}_7 + \text{K}_2\text{O}$) (dilué en oxydes libres) incluant les chromates, dichromates, molybdates, dimolybdates, tungstates et ditungstates de sodium et de potassium, pouvant se former dans des environnements contenant les éléments O-H-S-C-Cl et des sels alcalins. Les oxydes libres Na_2O et K_2O ont été inclus dans la phase liquide de façon à pouvoir prendre en compte les réactions du type $2 \text{A}_2\text{MO}_4 = \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$ (où $\text{A} = \text{Na}$ ou K , et $\text{M} = \text{Cr}$, Mo ou W).

Le modèle thermodynamique développé dans le cadre de ce projet va faciliter l'étude des phénomènes de formation des dépôts de cendres sur des alliages métalliques spécifiquement conçus pour résister aux conditions thermiques rigoureuses puisque la chimie combinée cendres/gaz/alliage contrôle le comportement de fusion des cendres formées.

La modélisation thermodynamique de type CALPHAD (CALculation of PHase Diagrams) constitue une méthode adaptée pour la prédiction des propriétés de fusion de phases inorganiques, en particulier pour la plupart des procédés de conversion d'énergie par voie thermique [43]. Elle repose sur une technique de minimisation de l'énergie de Gibbs du système, une fois que l'énergie de Gibbs a été définie pour chacune des phases pouvant potentiellement se former [28]. Il est indispensable de disposer d'un ensemble fiable et cohérent de données thermodynamiques expérimentales pour toutes les phases pertinentes afin de pouvoir prédire de manière satisfaisante

les équilibres de phases et les propriétés thermodynamiques du système multicomposant d'intérêt [28].

Dans le cadre de cette étude, une étude bibliographique approfondie relative aux chromates, dichromates, molybdates, dimolybdates, tungstates et ditungstates de sodium et de potassium a été réalisée pour les douze composés purs, et tous les sous-systèmes binaires et d'ordre supérieur pertinents : sous-systèmes binaires à ion commun impliquant au moins l'un de ces composés et un autre sel pertinent (NaCl , Na_2CO_3 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_7$, KCl , K_2CO_3 , K_2SO_4 , ou $\text{K}_2\text{S}_2\text{O}_7$), sous-systèmes ternaires à cation commun (Na^+ ou K^+), sous-systèmes ternaires réciproques (contenant les cations Na^+ et K^+ , et deux anions) et sous-systèmes d'ordre supérieur. Les données expérimentales jugées les plus fiables ont ensuite été utilisées pour calibrer le modèle thermodynamique.

Tous les articles scientifiques pertinents contenant des données expérimentales (équilibres de phases, enthalpies, capacités calorifiques, etc.) pouvant être utilisées pour la calibration du modèle ont été rassemblés et évalués de manière critique. Les structures cristallines des composés A_2MO_4 et $\text{A}_2\text{M}_2\text{O}_7$ (où $\text{A} = \text{Na}$ ou K , et $\text{M} = \text{Cr}$, Mo ou W) ont également été prises en compte lors de notre recherche bibliographique, car ces informations étaient importantes pour identifier la formation éventuelle de solutions solides avec les autres composés de sels considérés.

Pour tous les composés purs A_2MO_4 (où $\text{A} = \text{Na}$ ou K , et $\text{M} = \text{Cr}$, Mo ou W), des expériences de calorimétrie différentielle à balayage / thermogravimétrie (DSC-TGA) ont été menées au centre de recherche Åbo Akademi Process Chemistry Centre (en Finlande) pendant huit mois afin de pallier des données parfois limitées ou contradictoires. Pour chaque composé pur considéré, nous avons mesuré par DSC-TGA les températures et enthalpies des différentes transitions solide-solide, ainsi que la température et l'enthalpie de fusion. En outre, des analyses de diffraction des rayons X (DRX) à 25°C et à haute température (350 , 465 et 500°C) ont été réalisées afin d'identifier les structures cristallines et groupes d'espace des différents allotropes de K_2MoO_4 .

Finalement, des valeurs des propriétés thermodynamiques (enthalpie standard de formation $\Delta H_{298.15\text{ K}}^\circ$ à partir des éléments dans leur état standard stable à 298.15 K et 1 atm , entropie absolue (troisième loi) $S_{298.15\text{ K}}^\circ$ à 298.15 K et 1 atm , et capacité calorifique C_P en fonction de la température) ont été sélectionnées pour les composés purs Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, Na_2WO_4 , K_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$ et $\text{K}_2\text{W}_2\text{O}_7$.

Afin de pallier le manque de données expérimentales, des expériences de DSC-TGA ont été réalisées à différentes compositions pour plusieurs sous-systèmes binaires à ion commun. Cela nous a permis de mieux caractériser les équilibres de phases (en particulier, les équilibres de phases solide-solide). En ce qui concerne les chromates, les expériences de DSC-TGA ont été réalisées pour les sous-systèmes binaires à ion commun ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4$), ($\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4$) et ($\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$), ainsi que pour le sous-système ternaire à cation commun ($\text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4$) pour lequel aucune donnée expérimentale n'était disponible. Nous avons ainsi pu vérifier la présence d'un eutectique ternaire, correspondant à la formation d'une phase liquide à basse température et donc associé à un risque de corrosion « catastrophique ».

En ce qui concerne les molybdates, les expériences de DSC-TGA ont été effectuées pour les sous-systèmes binaires à ion commun ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{MoO}_4$), ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$), ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$), ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$), ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{MoO}_4$) et ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$).

Finalement, des mesures de DSC-TGA ont également été effectuées pour plusieurs sous-systèmes binaires à ion commun à base de tungstates. Malheureusement, en raison de contraintes de temps, la modélisation thermodynamique de ces systèmes n'a pas pu être finalisée dans le cadre de cette thèse, et les données expérimentales obtenues n'ont donc pas été décrites dans ce mémoire. Ce travail sera terminé ultérieurement.

Les phases non-stoechiométriques de glasérite de chrome $\text{K}_3\text{Na}(\text{CrO}_4)_2$ et de glasérite de molybdène $\text{K}_3\text{Na}(\text{MoO}_4)_2$ (stable au-dessus de 240°C [44]) ont été étudiées à l'aide de la microscopie électronique à balayage (MEB), de la spectroscopie de rayons X à dispersion d'énergie (EDS) et de la DSC-TGA. Pour la glasérite de chrome, un mélange mécanique de composition (45% molaire Na_2CrO_4 + 55% molaire K_2CrO_4) a été recuit à 400°C pendant trois semaines, puis un excès de Na_2CrO_4 ou K_2CrO_4 a été ajouté. De manière similaire, pour la glasérite de molybdène, un mélange mécanique de composition (35% molaire Na_2MoO_4 + 65% molaire K_2MoO_4) a été recuit à 400°C pendant quatre semaines, avec l'ajout subséquent d'un excès de Na_2MoO_4 ou K_2MoO_4 .

Le Modèle Quasichimique Modifié dans l'Approximation des Quadruplets (MQMQA) [45] a été utilisé pour modéliser la phase liquide réciproque ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) (diluée en oxydes libres) et la solution solide hexagonale hP22 de haute température ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4 + [\text{K}_2\text{MoO}_4]$), diluée en K_2MoO_4 et avec une solubilité mutuelle complète pour les autres sels. Le MQMQA prend en compte simultanément l'ordre à courte distance entre les ions premiers voisins (cation-anion) et entre les ions seconds voisins (cation-cation et anion-anion). Toutes les autres solutions solides ont été modélisées avec le « Compound Energy Formalism » (CEF) [46-48].

Une approche de type CALPHAD (CALculation of PHase Diagrams) [49, 50] a été adoptée pour développer le modèle thermodynamique. Des équations de modèles permettant de décrire l'énergie de Gibbs de chaque phase ont été obtenues en fonction de la température, et aussi de la composition (dans le cas de la solution liquide et des différentes solutions solides).

Des prédictions ont pu et pourront ainsi être faites pour le système multicomposant d'intérêt à partir des paramètres de modèles obtenus pour les sous-systèmes binaires à ion commun, les sous-systèmes ternaires à cation commun (Na^+ ou K^+) et les sous-systèmes ternaires réciproques (avec les cations Na^+ et K^+ , et deux anions), et à l'aide de techniques d'interpolation appropriées.

Les propriétés thermodynamiques et les équilibres de phases ont été calculés à l'aide du logiciel thermochimique FactSage [42], qui inclut un algorithme de minimisation de l'énergie de Gibbs du système.

Le modèle thermodynamique développé permet de réaliser des calculs d'équilibres de phases dans le système multicomposant ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) (dilué en oxydes libres), d'où une meilleure compréhension des phénomènes de corrosion à haute température tout en évitant une approche expérimentale fastidieuse et coûteuse basée sur des essais et erreurs.

Cette thèse est présentée dans un format dit « par articles ». Le contenu scientifique de ce travail

est ainsi présenté sous la forme de quatre articles principaux (tous soumis pour publication dans des journaux avec comité de lecture), et d'un article de conférence déjà publié (annexe A).

Le présent chapitre (**chapitre 1**) a présenté le contexte général, les différents domaines impliqués et la problématique de notre étude, portant sur la corrosion chaude dans les installations de conversion d'énergie par combustion. Il a également décrit les études antérieures réalisées, l'objectif de notre recherche, les méthodologies utilisées pour y parvenir, ainsi que la contribution de cette recherche à la communauté scientifique.

Le **chapitre 2** consiste en une revue de la littérature décrivant de manière générale la corrosion chaude. Il aborde l'histoire de ce phénomène, les deux types de corrosion à haute température, ainsi que les mécanismes potentiels pouvant être impliqués en fonction des espèces corrosives.

Le **chapitre 3** est consacré à la description des deux modèles (MQMQA et CEF) utilisés pour la modélisation de la solution liquide et des solutions solides du système multicomposant d'intérêt, ainsi qu'à la description des techniques d'interpolation relatives aux sous-systèmes ternaires à cation commun (Na^+ ou K^+).

Le **chapitre 4** énumère les objectifs de notre étude et met en évidence la cohérence entre les différents articles.

Le **chapitre 5** (article soumis pour publication dans « Journal of Physical and Chemical Reference Data ») décrit en détail les propriétés thermodynamiques sélectionnées pour les composés purs Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 et K_2WO_4 , à partir des données issues de la littérature et de nos résultats de DSC-TGA et DRX.

Le **chapitre 6** (article lui-aussi soumis pour publication dans « Journal of Physical and Chemical Reference Data ») présente les propriétés thermodynamiques sélectionnées pour les composés purs $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{W}_2\text{O}_7$ et $\text{K}_2\text{W}_2\text{O}_7$, en se basant sur les données disponibles dans la littérature.

Le **chapitre 7** (article soumis pour publication dans « Chemical Engineering Science ») décrit le modèle thermodynamique développé pour le système ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{O}$) (dilué en oxydes libres), plus particulièrement l'ajout des constituants Na_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, K_2CrO_4 et $\text{K}_2\text{Cr}_2\text{O}_7$ au modèle antérieur de Lindberg et al [39-41].

Le **chapitre 8** (article soumis pour publication dans « Industrial & Engineering Chemistry Research ») présente le modèle thermodynamique développé pour le système ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) (dilué en oxydes libres), plus particulièrement l'ajout des constituants Na_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, K_2MoO_4 et $\text{K}_2\text{Mo}_2\text{O}_7$ au modèle décrit dans le chapitre 7.

Le **chapitre 9** énumère l'ensemble des résultats obtenus ainsi que les contributions scientifiques pertinentes réalisées dans le cadre de cette thèse.

Dans le dernier chapitre de cette étude, le **chapitre 10**, une évaluation détaillée du travail accompli est présentée, accompagnée d'une perspective sur les développements futurs potentiels. Ce chapitre explore également les opportunités de recherche à venir dans le domaine de la modélisation de la corrosion à haute température.

CHAPITRE 2 REVUE DE LA LITTÉRATURE

2.1 Généralités, contexte d'étude et problématique

La plupart des installations industrielles de combustion, telles que mentionnées dans le chapitre précédent, sont conçues à partir d'acier et d'aciers inoxydables alliés à du Ni, Cr, Mo, W et V [19-23]. Ces matériaux sont reconnus pour leur résistance à la corrosion et pour leur capacité à supporter des températures assez élevées de mise en service, ce qui en fait des candidats potentiels pour la fabrication des tubes de surchauffeurs de chaudière. Toutefois, ils sont sujets à des conditions extrêmes, à des températures supercritiques et à des atmosphères chimiques hostiles. De telles conditions peuvent entraîner une oxydation accélérée de ces matériaux, en particulier lorsqu'une fine couche de sel fondu se forme à la surface du métal, résultat de la condensation de vapeurs issues du combustible et de l'entraînement par convection de particules fines. Ce phénomène est connu sous le nom de corrosion chaude.

Il est important au préalable de mentionner que le terme "corrosion" vient du latin (*corrosio*, corroder) et signifie "ronger", "attaquer". En effet, la dégradation de substances ou d'interfaces est la conséquence d'une destruction progressive par des réactions chimiques [51]. Plus précisément, on parle d'une : « *réaction d'un matériau pouvant induire une détérioration de la fonction d'un composant ou d'un système complexe. Dans la plupart des cas, cette réaction est de nature électrochimique. Dans certains cas, elle peut être (non électrochimique) chimique ou de nature physique* ».

À des températures relativement élevées, la dégradation des matériaux peut être provoquée soit par l'action de gaz corrosifs tels que O_2 , S_2 , SO_2 , H_2O et CO_2 , résultant alors en une oxydation du métal ou de l'alliage (connue sous le nom de "**corrosion sèche**" ou "**oxydation à haute température**"[52]), soit par interaction avec des sels fondus, pouvant provoquer la dissolution partielle ou totale de la couche d'oxyde protectrice (connue sous le nom de "**corrosion chaude**" ou "**fluxage**" [53]).

Dans ce projet de thèse, notre attention s'est portée sur la corrosion chaude.

2.2 Définition de la corrosion chaude

La corrosion chaude est une oxydation accélérée survenant à haute température, généralement entre 600 et 950°C, en présence de sels tels que Na_2SO_4 , NaCl , V_2O_5 , etc. Des dépôts se forment en présence d'autres phases gazeuses autour du métal, entraînant la détérioration des couches d'oxyde protectrices à la surface du métal [14, 54].

2.3 Historique de la corrosion chaude

La corrosion par des sels fondus a été rapportée pour la première fois au début des années 1940 sur les tubes des chaudières des centrales thermiques alimentées au charbon. Par la suite, elle a été observée pour les moteurs à combustion interne, les turbines, les incinérateurs et les chaudières d'ordures ménagères industrielles [14]. Cette situation s'est manifestée chez les fabricants et les exploitants d'éoliennes à la fin des années 1960, lorsque les moteurs d'hélicoptères et d'avions de sauvetage ont été gravement endommagés pendant la guerre du Vietnam.

Les premières publications techniques [55] ont fait ressortir la réactivité de la sulfuration des métaux par Na_2SO_4 ainsi que l'oxydation accélérée d'un eutectique à base de sulfures. Ce mécanisme s'appelait au départ sulfuration.

Des études ultérieures ont démontré que les sulfures se formaient à la suite de réactions de substrats métalliques en contact avec une fine couche de sel fondu de sulfate de sodium [56].

2.4 Types de corrosion chaude

La corrosion chaude se manifeste sous deux formes différentes [14, 57, 58] détaillées ci-dessous.

2.4.1 La corrosion à haute température (« HTHC »)

Ce phénomène se produit à des températures allant de 800 à 950°C. D'abord, les sels alcalins fondus précipitent à la surface du métal. Cette précipitation est suivie d'un cycle de réactions chimiques affectant d'abord le film d'oxyde protecteur, puis se poursuivent jusqu'à ce que le chrome soit entièrement éliminé du matériau de base.

Une fois le chrome appauvri, le matériau de base s'oxyde davantage, entraînant la formation d'un

dépôt poreux [14].

2.4.2 La corrosion à basse température (« LTHC »)

Ce type de corrosion survient entre 600 et 800°C, et se caractérise par la formation de piqûres dues à la présence de mélanges de sels à bas point de fusion; ce qui entraîne une diminution du point de fusion via un eutectique. Par ailleurs, la couche d'oxyde est parfois altérée à certains endroits suite à des attaques localisées de chlorure ou à l'érosion. Cela peut conduire à la formation de fissures ou de crevasses dans lesquelles les sels peuvent être piégés localement [14].

En raison de la faible solubilité de la couche d'oxyde et de la faible probabilité que le dépôt initial soit à l'état liquide, le fluxage de la couche d'oxyde est très incertain. Il est nécessaire, dans ces conditions, de prendre en compte les risques potentiels de détérioration du métal sous-jacent [54].

Les installations de combustion de la biomasse ou d'incinération des déchets sont généralement soumises à des températures inférieures à 600°C. Pour la combustion du charbon, en revanche, les températures au niveau des surchauffeurs sont parfois très élevées. Quant à la combustion de la liqueur noire, les températures typiques se situent autour de 500°C. Le seuil de ces températures est déterminé par la plus basse température de fusion des cendres émises.

2.5 Corrosion par des sels fondus

Les centrales thermiques requièrent en permanence des combustibles organiques pour leur fonctionnement. Ces combustibles sont riches en impuretés telles que le chlore, le soufre, le potassium, le sodium, le zinc, le plomb et d'autres métaux lourds [59]. La nature de ces impuretés varie suivant le type d'installation. Par exemple, les usines de gazéification du charbon contiennent une forte proportion de soufre atmosphérique, de sodium et de potassium, tandis que le chlore est moins présent [4].

Les espèces chimiques les plus agressives dans les centrales thermiques au charbon sont les métaux alcalins (Na, K), que l'on retrouve notamment sous forme de sulfates. En revanche, dans les surchauffeurs d'ordures ménagères, ces métaux alcalins sont présents sous forme de chlorures [7, 60]. Dans la plupart des cas, les sulfates tels que K_2SO_4 et Na_2SO_4 se déposent sur les parties les plus chaudes, alors que les chlorures, plus volatils, se déposent sur les parties les plus froides [61].

Par ailleurs, la chaudière de récupération de pâte kraft est principalement composée d'un mélange de Na_2S , Na_2CO_3 et Na_2SO_4 , avec de faibles quantités de K, Cl et OH ainsi que divers anions de soufre tels que S_n^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ et $\text{S}_2\text{O}_7^{2-}$ [62].

La combustion génère des gaz très agressifs et corrosifs (cendres volantes) avec des composants à bas point de fusion. Ces derniers forment des dépôts corrosifs à la surface des tubes des surchauffeurs, des parois des réservoirs d'eau, des tubes des fours, des évaporateurs et d'autres tubes d'économiseurs [14, 63]. Ces dépôts peuvent réduire le gain d'énergie en raison du faible transfert de chaleur vers la vapeur contenue dans les tubes.

Les dépôts formés sont des composés ioniques solides ou liquides, généralement appelés sels.

Le terme "sel fondu" est souvent utilisé pour désigner les phases liquides ioniques à haute température, tandis que le terme "liquide ionique" est principalement utilisé pour les liquides de nature ionique à basse température ou à température ambiante [28].

Les mélanges de sels intervenant dans les différents procédés industriels évoqués dans le chapitre 1 (Introduction) sont constitués d'un ensemble de cations et d'anions, définis de la manière suivante :

Na^+ , K^+ , (Cr^{2+} , Cr^{3+} , Cr^{6+}), (Mo^{2+} , Mo^{3+} , Mo^{4+} , Mo^{5+} , Mo^{6+}), (W^{2+} , W^{3+} , W^{4+} , W^{5+} , W^{6+}), (V^{2+} , V^{3+} , V^{4+} , V^{5+}) || Cl^- , S_n^{2-} ($n = 1, 8$), SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_7^{2-}$, CO_3^{2-} , C^{4-} , C_2^{2-} , H^- , OH^- , (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$), (MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$), (WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$), (VO_4^{2-} , $\text{V}_2\text{O}_7^{2-}$), (O^{2-} , O_2^{2-} , O_3^{2-}).

La modélisation thermodynamique menée dans le cadre de ce projet doctoral ne tient pas compte des deux anions VO_4^{2-} et $\text{V}_2\text{O}_7^{2-}$ intervenant dans la corrosion associée aux vanadates, étant donné que les données relatives aux mécanismes de corrosion et les données thermodynamiques nécessaires à la calibration de notre modèle sont extrêmement limitées, voire inexistantes.

À titre d'exemple, considérons Na_2SO_4 , K_2SO_4 , NaCl , KCl et V_2O_5 , qui sont tous impliqués dans le système chimique présenté ci-dessus. Ces composés ont un faible point de fusion, et peuvent donc être présents sous forme liquide lors des processus de combustion ou de gazéification (voir le Tableau 2.1).

Tableau 2.1 Températures de fusion de sels alcalins et de l'oxyde de vanadium [63, 64]

	KCl	NaCl	Na ₂ SO ₄	V ₂ O ₅
$T_{\text{fusion}} (^{\circ}\text{C})$	772	801	884	691

2.6 Mécanismes de corrosion en fonction des espèces corrosives

2.6.1 En présence des gaz de combustion

Dans des environnements d'incinération, les principaux agents corrosifs sont le chlore (Cl₂, HCl) et le soufre (SO₂, SO₃). Les gaz de combustion contiennent en outre du CO₂ et du H₂O provenant de la combustion de matières organiques.

Le Tableau 2.2 illustre la composition des gaz dans les différentes parties d'un incinérateur [60].

Tableau 2.2 Composition des gaz de combustion dans les différentes parties d'un incinérateur (TIRU) [60]. Adapté avec permission

Gaz	O ₂ (%)	H ₂ O(%)	CO ₂ (%)	HCl ppm	SO ₂ ppm	HF ppm	CO ppm
Bas de la chambre de combustion	6			40-1650	90-200	10-40	> 1000
Après injection d'air secondaire	20	8-14			1-6	très faible	
Haut de chambre de combustion-surchauffeur	8-10	15	9-12	600-1200	90-130	< 20	20-40

Tableau 2.3 Analyse des gaz évacués par la chaudière dans diverses installations [60]. Adapté avec permission

Gaz	O ₂ (%)	CO ₂ (%)	CO (ppm)	SO ₂ (ppm)	HCl (ppm)	H ₂ O (%)
Oberhausen (Allemagne)				87	399	
	10.4-10.7	8.6-10.4	15-56	26-65	798-1300	17.4-18
	7.8-8	11-12.2	1-2	13	600-690	17.4-18
Japon	10-11.6	8.9-9.5	100-123	< 0.01	422-641	16.6-17.7
	7.9-9	10.9-12.3		19	1060-1250	19.5-21
Harrisburg (USA)	9	7.5	30	135	485	8.8
Miami (USA)	9.5	8.4	10	107	374	10.5
AKren (USA)	9.9	9	< 20	116	284	14.2
Högdalen (Suède)	5.7-9.9	9.5-13.9	22-68	38-71	455-680	
Autriche	13		25	150	260	
	9	13	20	500	690	

Le Tableau 2.3 présente la composition des gaz émis par les chaudières de diverses usines. On constate que les principaux agents corrosifs sont HCl et SO₂, dont les concentrations moyennes atteignent environ 500 ppm et 50 ppm, respectivement. Cette composition sert de référence dans

les essais de corrosion pour le choix de l'alliage [60].

Il est possible que la composition du gaz ne soit pas uniforme dans toute l'installation en raison des injections locales d'air et des variations de température selon l'emplacement [65].

2.6.1.A Espèces chlorées

Le chlore est fréquemment présent sous diverses formes, telles que le chlorure d'hydrogène (HCl), le dichlore (Cl₂), contenu dans les dépôts de cendres volantes [66], ou les chlorures alcalins (NaCl, KCl). Ces composés contribuent généralement aux problèmes de corrosion des surchauffeurs [67]. En effet, les gaz HCl et Cl₂ peuvent se condenser sur les cendres et les surfaces froides, notamment les tubes échangeurs de chaleur, en formant des eutectiques à bas point de fusion (tel que KCl-ZnCl₂) [68]. Cette condensation entraîne une augmentation du taux de détérioration des matériaux, en raison de la formation d'une phase liquide.

2.6.1.B Espèces soufrées

Le soufre en conditions oxydantes est présent sous forme de SO₂ et de SO₃. Les pressions partielles de ces derniers sont déterminées suivant cet équilibre :



La conversion de SO₂ en SO₃ au niveau des dépôts et des interfaces alliage/oxyde dépend donc de la pression d'oxygène [60].

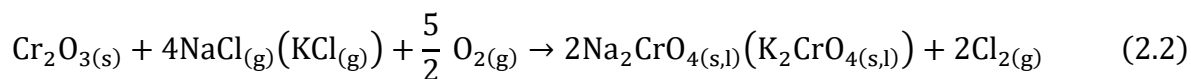
La présence de soufre gazeux peut également conduire à la formation de composés fondus tels que les sulfates (SO₄²⁻) et les pyrosulfates (S₂O₇²⁻) ayant de basses températures de fusion [69]. Ces aspects seront abordés dans les sections suivantes.

2.6.2 Corrosion associée aux chlorures alcalins gazeux

Les cendres formées lors de la combustion sont des combinaisons d'anions relativement simples (Cl⁻, SO₄²⁻, CO₃²⁻, O₂⁻, S₂⁻) et de cations métalliques. Ces mélanges de sels ont de très fortes

concentrations en chlorures alcalins et en sulfates, et sont principalement riches en sels de **potassium** (KCl et K₂SO₄) [43, 70].

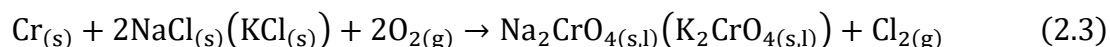
Les couches d'oxyde de chrome (Cr₂O₃) garantissent une protection efficace contre la corrosion induite par le chlore mais, en présence de NaCl/KCl gazeux, elles se décomposent facilement en se transformant en chromate de sodium ou de potassium [70] selon la réaction ci-dessous:



2.6.3 Corrosion associée aux chlorures alcalins solides

Les dépôts tels que NaCl, KCl et K₂SO₄ peuvent entraîner une corrosion très sévère, même à des températures inférieures au point de fusion des sels purs. Certaines expériences de corrosion ont montré que la formation de K₂CrO₄ ou Na₂CrO₄ était plus stable et pouvait se produire à des teneurs en chlorure plus élevées [70].

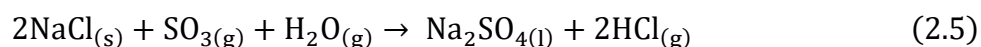
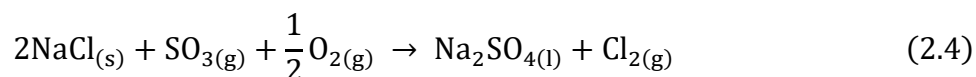
La présence de pressions partielles élevées de substances chlorées produites peut générer une attaque de corrosion en phase gazeuse. Des réactions peuvent en outre se produire dans les dépôts, conduisant à la transformation de KCl en Cl₂:



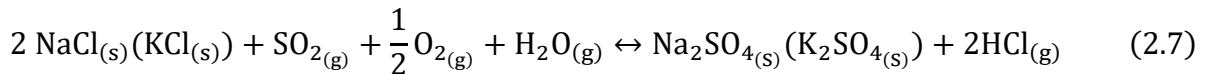
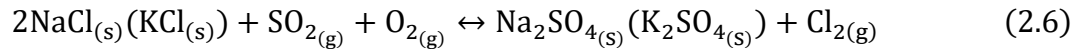
2.6.4 Corrosion par la sulfatation des chlorures alcalins

Les dépôts sulfatés dans les turbines marines contiennent parfois du chlorure de sodium; ce qui entraîne la diminution du point de fusion de Na₂SO₄ [24]. Quant aux turbines industrielles, elles contiennent généralement du **vanadium**, du **calcium**, du **potassium**, du **manganèse** et du **fer** [24].

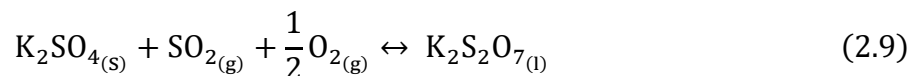
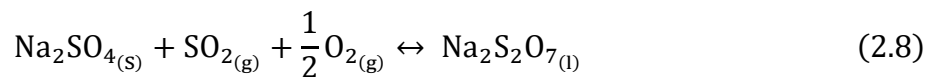
Le dépôt le plus fréquemment formé est le sulfate de sodium, issu de l'interaction entre le soufre et le sodium contenus dans l'air sous forme de poussières. Les réactions de sulfatation ci-dessous sont à l'origine de son apparition :



Les dépôts de sulfate de sodium peuvent considérablement accentuer la corrosion même si le chlorure de sodium additionné au sulfate de sodium ne représente que 1% du poids de ce dernier [70]:



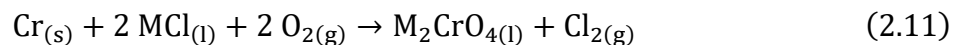
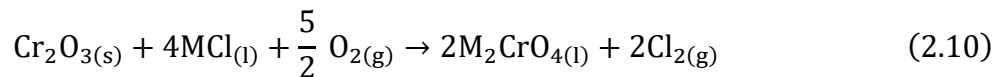
De même, les pyrosulfates tels que $\text{Na}_2\text{S}_2\text{O}_7$ et $\text{K}_2\text{S}_2\text{O}_7$ ont un rôle important dans la corrosion de basse température, comme le montrent les réactions suivantes [71] :



Dans ce contexte, il est possible de former du $\text{K}_2\text{S}_2\text{O}_7$ à 538°C à partir d'au moins 100 000 ppm de SO_3 , et à 593°C à partir d'environ 35 000 ppm de SO_3 [24].

2.6.5 Corrosion associée aux chlorures alcalins fondus

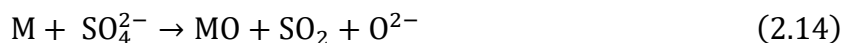
Les mécanismes de corrosion intervenant en phase fondue sont similaires à ceux présentés pour les chlorures alcalins solides [70]. Le Cr_2O_3 se transforme en chromate en présence de NaCl-KCl fondu. Les réactions correspondantes sont les suivantes :



Avec $\text{M} = \text{K}$ ou Na .

2.6.6 Corrosion associée aux sulfates alcalins fondus

Les espèces corrosives **d'oxygène** dans les **sulfates fondus** sont issues de la dissociation de l'ion sulfate dans le dépôt fondu [70] comme l'illustrent les réactions suivantes :



Lorsque l'activité de O_2 augmente à l'interface oxyde/métal, la dissolution basique de la couche d'oxyde se produit suivant les réactions ci-après [72] :



Et/ou



En présence de sulfate fondu, SO_3 se dissout facilement dans la masse fondue sous forme de pyrosulfate, selon la réaction suivante [70] :



2.6.7 Corrosion due aux carbonates alcalins fondus

Les caractéristiques chimiques des carbonates fondus diffèrent de celles des sulfates fondus, et les mécanismes de corrosion de ces deux composés sont complètement différents [70]. Les interactions entre O_2 et CO_3^{2-} à la surface de dépôt fondu produisent des anions d'oxygène selon la réaction ci-dessous [73] :



Ils se réduiront ensuite, au contact du métal, en O_2^{2-} selon les réactions suivantes :



Ces derniers interviennent dans le processus d'oxydation du métal (dissolution basique) au contact des dépôts de carbonates fondus :



Les dépôts d'oxyde peuvent également être dissous selon la réaction suivante :



Par ailleurs, le fluxage peut avoir lieu soit par la combinaison d'oxydes avec O^{2-} pour former des anions (flux basique), soit par la décomposition des oxydes en cations correspondants et en O^{2-} (flux acide) [14].

On parle de flux acide lorsque l'activité de O^{2-} est considérablement réduite dans le sel fondu [14]. Par conséquent, cette oxydation est considérablement plus sévère que celle du flux basique [14].

Les anions O_2^{2-} et O_3^{2-} ne sont donc pas pris en considération dans notre modèle puisque leur présence est improbable.

2.6.8 Corrosion en atmosphère très réductrice

Dans des conditions très réductrices, certaines zones des installations peuvent manquer d'air nécessaire à l'incinération. Par conséquent, une combustion incomplète survient, entraînant la formation de produits de combustion incomplète, principalement du CO [65]. Outre le CO, d'autres éléments tels que l'hydrogène (H) et l'hydroxyde (OH) peuvent également être présents en petites quantités.

Notons que les anions C^{4-} et C_2^{2-} ne sont pas pris en compte dans notre modèle, car leur présence est peu probable. En effet, ces ions sont généralement instables et ne sont pas connus pour induire un problème de corrosion chaude.

2.7 Exemple typique de corrosion chaude dans les installations de fabrication du papier kraft

Pour illustrer notre propos, prenons l'exemple de la corrosion pouvant survenir lors du procédé de fabrication du papier kraft. Ce cas a été décrit dans notre article de conférence REWAS 2022 : Energy Technologies and CO₂ Management (Volume II) (voir l'annexe A) [74].

La chaudière de récupération peut subir une corrosion extrême en raison de la présence de sels fondus tels que Na_2CO_3 et Na_2S issus de la combustion de la liqueur noire [74]. La présence

éventuelle d'autres résidus de combustion tels que les mélanges de sulfate de sodium, de carbonate de sodium et de chlorure de sodium, de même que des gaz corrosifs, peuvent également contribuer à ce phénomène [74].

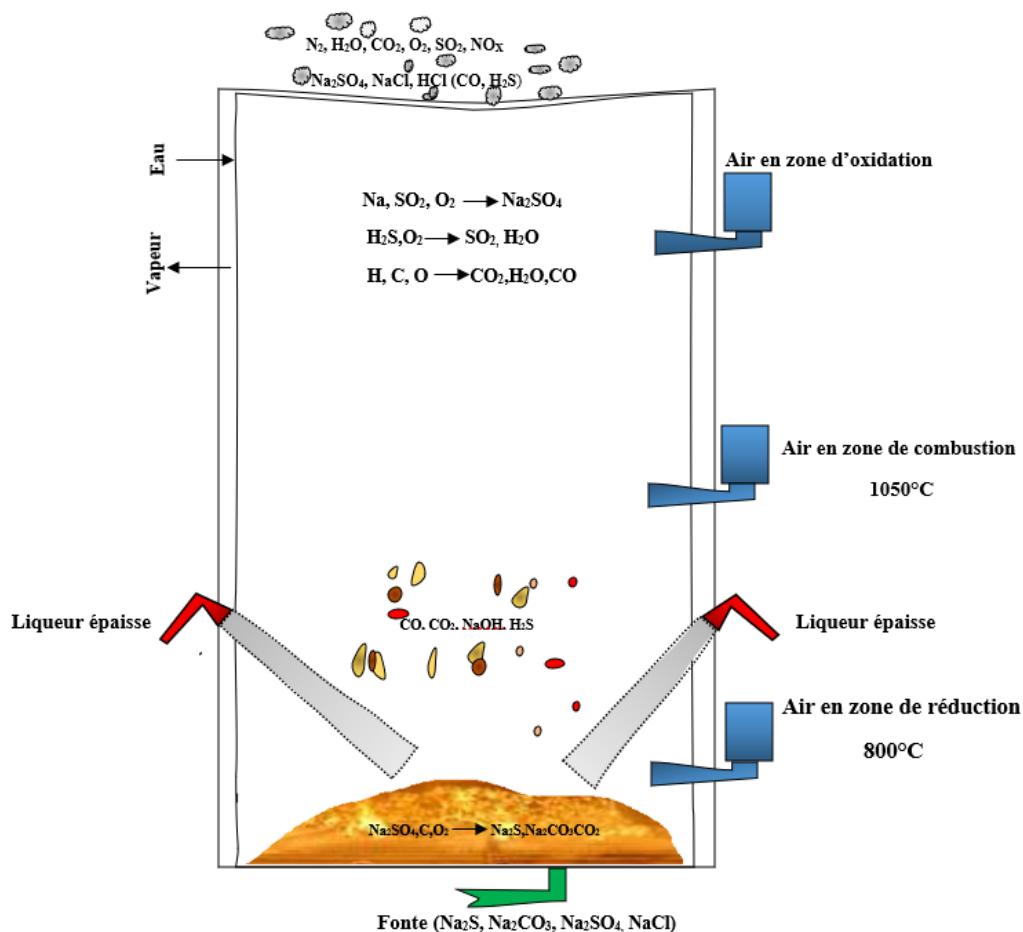


Figure 2.1 Réactions chimiques au niveau d'une chaudière de récupération. Adapté avec permission [74]

Les principales réactions susceptibles de se manifester dans une chaudière de récupération sont décrites dans la Figure 2.1. En effet, il peut y avoir formation de traces de sulfure d'hydrogène lors de la réduction du soufre en sulfure. Ceci survient si l'alimentation en air est insuffisante ou si le mélange d'air est incomplet. Ces traces de sulfure d'hydrogène peuvent être émises dans les gaz de combustion [74].

Il est également fréquent que des dépôts se détachant des parois du four entraînent le dégagement instantané de grandes quantités de sulfure d'hydrogène [74].

Les gaz tels que la vapeur d'eau, le dioxyde de carbone, l'oxygène, le sulfure d'hydrogène (H_2S) et le dioxyde de soufre (SO_2) sont responsables de la corrosion des tubes supérieurs et des surchauffeurs. Généralement, le dioxyde de soufre intervient en phase gazeuse avec le sodium pour former du sulfate de sodium [74].

Par ailleurs, le sulfure, en grande partie sous la forme de sulfate de sodium, entraîne la diminution des émissions de dioxyde de soufre [74].

Durant le procédé, la température du four tend à croître au fur et à mesure que la quantité de matière sèche dans la liqueur noire augmente [74]. Il en résulte une diminution des émissions de sulfure d'hydrogène et une augmentation des émissions de sodium [74].

2.8 Corrosion chaude des éléments d'alliage (Cr, Mo, W et V)

2.8.1 Chromates et dichromates

Les mécanismes de corrosion chaude faisant intervenir les chromates et les dichromates de sodium et de potassium ont été répertoriés dans nos travaux (voir annexe A et publications aux chapitres 5, 6 et 7).

Le revêtement protecteur à base de Cr_2O_3 peut subir une série de réactions de corrosion au contact du NaCl et/ou du KCl issus des procédés de combustion; ce qui entraîne la formation de Na_2CrO_4 et/ou de K_2CrO_4 tel que rapporté dans [31, 74, 75]. Ces réactions peuvent conduire à une oxydation supplémentaire du chrome, lequel passe de l'état d'oxydation III à l'état d'oxydation VI [74]. La libération des chlorures a en outre un impact direct sur la couche d'oxyde protectrice; ce qui endommage fortement l'acier [74].

Par ailleurs, une interaction entre KCl et Cr conduit à la formation de dichromate de potassium ($\text{K}_2\text{Cr}_2\text{O}_7$) [34, 75]. Ce mécanisme implique également la formation de mélanges eutectiques entre K_2CrO_4 et KCl [43]. Les mélanges de ce type ont des points de fusion inférieurs à ceux des composés purs [74].

À titre d'illustration, considérons le diagramme de stabilité du chrome en contact avec $\text{KCl}_{(s)}$ dans un environnement surchauffé à 500°C en fonction de $p(\text{H}_2\text{O})$ et $p(\text{HCl})$ à une pression partielle d'oxygène $p(\text{O}_2) = 0.1$ bar, établi par Lindberg et al [43]. Il en ressort que, dans ces conditions,

$\text{Cr}_2\text{O}_{3(s)}$ réagit avec la phase liquide riche en $\text{K}_2\text{Cr}_2\text{O}_{7(l)}$ et en $\text{KCl}_{(l)}$ avant la formation de $\text{K}_2\text{CrO}_{4(s)}$ [43].

2.8.2 Molybdates et dimolybdates

Les mécanismes de corrosion chaude associés aux molybdates et dimolybdates de sodium et de potassium ont été répertoriés dans l'annexe A, de même que dans nos travaux présentés dans les publications des chapitres 5 et 8. La corrosion catastrophique observée dans les superalliages à base de Mo est a priori liée au fluxage provoqué par la formation de MoO_3 à l'interface métal/dépôt [31]. Or, à ce jour, les mécanismes intervenant dans la formation de Na_2MoO_4 et des mélanges $\text{Na}_2\text{MoO}_4\text{-MoO}_3$ et $\text{Na}_2\text{MoO}_4\text{-2MoO}_4$ n'ont pas encore été complètement identifiés [31, 74].

Par ailleurs, des analyses ont été effectuées à une température de 900°C pour étudier l'oxydation des superalliages à base de nickel Fe-25Ni-16Cr-6Mo (avec une teneur en Mo de plus de 3%). Celles-ci ont révélé une corrosion catastrophique du métal engendrée par une accumulation importante de MoO_3 gazeux à la surface du matériau [74].

Lors d'une étude menée dans une même chambre de réaction, il a été constaté que l'alliage Ni-15%Cr revêtu de Na_2SO_4 présentait des comportements de corrosion sévères similaires à ceux des alliages Ni-15Cr-Mo. Cette observation suggère que MoO_3 s'est dissous dans la couche de sel et a ensuite été entraîné dans la phase vapeur [76].

La littérature existante ne décrit pas les mécanismes réactionnels correspondant aux molybdates de potassium ainsi qu'aux dimolybdates de sodium et de potassium.

2.8.3 Tungstates et ditungstates

Une corrosion catastrophique peut survenir suite à la présence de Na_2WO_4 . La couche de sel formée est constituée d'un oxyde très acide, WO_3 , et provoque la dissolution automatique de la couche d'oxyde protectrice [74].

Par ailleurs, en présence d'une forte concentration d'oxygène dans l'environnement, une interaction entre le sodium et le tungstène pourrait entraîner la formation de $\text{Na}_2\text{W}_2\text{O}_7(\text{s})$ [34].

Les mécanismes réactionnels relatifs au tungstate et au ditungstate de potassium ne sont pas encore répertoriés dans la littérature.

2.8.4 Vanadates

La connaissance des mécanismes de corrosion chaude en présence de vanadates demeure assez limitée. Tel que décrit dans l'annexe A [74], en présence de dépôts de vanadates fondus, on peut constater des risques de dissolution de la couche protectrice de Cr_2O_3 [74]. La dissolution automatique de l'oxyde protecteur est induite par la forte acidité de V_2O_5 [74]. En effet, en présence de vanadates, certains oxydes peuvent former des solutés acides ayant une solubilité considérablement accrue. Ceci entraîne une attaque plus rapide des oxydes par les mélanges fondus de sulfate-vanadate que par les sulfates fondus seuls [74].

2.9 Système de sels modélisé dans cette étude

Une base de données thermodynamiques **FTpulp** [42] a été développée précédemment par Lindberg et al [39-41] pour les sels alcalins intervenant dans les procédés de combustion du papier kraft et de la biomasse. Ce modèle considère les cations Na^+ et K^+ , et les anions CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, S_n^{2-} ($n=1-8$), et Cl^- .

Les mélanges de sulfures alcalins, de sulfates alcalins acides et de polysulfures alcalins ont aussi été considérés. À ce jour, les produits de corrosion associés aux éléments d'alliage Cr, Mo, W et V n'ont pas été pris en compte.

Suite aux différentes évaluations que nous avons menées sur la corrosion par des sels fondus à haute température et suite aux travaux antérieurs de Lindberg et al [28, 39-41, 43], le système chimique simplifié indiqué ci-dessous pourrait être considéré :

$\text{K}^+, \text{Na}^+, (\text{Cr}^{2+}, \text{Cr}^{3+}, \text{Cr}^{6+}), (\text{Mo}^{2+}, \text{Mo}^{3+}, \text{Mo}^{4+}, \text{Mo}^{5+}, \text{Mo}^{6+}), (\text{W}^{2+}, \text{W}^{3+}, \text{W}^{4+}, \text{W}^{5+}, \text{W}^{6+}) \parallel \text{Cl}^-, \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}, \text{SO}_3^{2-}, \text{CO}_3^{2-}, (\text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}), (\text{MoO}_4^{2-}, \text{Mo}_2\text{O}_7^{2-}), (\text{WO}_4^{2-}, \text{W}_2\text{O}_7^{2-}), \text{O}^{2-}$.

Finalement, le système modélisé dans le cadre de cette étude est le suivant :

$\text{K}^+, \text{Na}^+ \parallel \text{Cl}^-, \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}, \text{CO}_3^{2-}, (\text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}), (\text{MoO}_4^{2-}, \text{Mo}_2\text{O}_7^{2-}), \text{O}^{2-}$ (où les ions O^{2-} sont présents en quantités diluées).

L'objectif de ce projet de doctorat était de développer un nouveau modèle thermodynamique permettant de prédire la formation de dépôts et de sels fondus corrosifs, en commençant par l'ajout des ions chromates et dichromates au modèle pour le système $\text{Na}^+, \text{K}^+ \parallel \text{Cl}^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}$ précédemment développé par Lindberg et al. Les ions molybdates et dimolybdates ont eux-aussi été ajoutés dans le cadre de ce travail.

Par manque de temps, les sous-systèmes binaires et d'ordre supérieur à base de tungstates et de ditungstates n'ont malheureusement pas pu être finalisés.

CHAPITRE 3 MODÉLISATION THERMODYNAMIQUE

Nous avons adopté l'approche CALPHAD pour la modélisation thermodynamique. Cette approche nous a permis d'obtenir un ensemble de fonctions d'énergie de Gibbs pour toutes les phases du système multicomposant étudié en fonction de la température et de la composition.

La Figure 2 de l'annexe A présente une brève description de cette méthode sous la forme d'un organigramme. Dans un premier temps, nous avons effectué une recherche bibliographique approfondie afin de rassembler toutes les données expérimentales disponibles pour calibrer notre modèle thermodynamique. Nous avons ensuite sélectionné les données les plus fiables et procédé à la modélisation thermodynamique. Le MQMQA a été utilisé pour modéliser la phase liquide et la solution solide hexagonale hP22 de haute température. Pour toutes les autres solutions solides, nous avons utilisé le CEF. Ces modèles sont décrits en détail aux chapitres 7 et 8, et sont seulement abordés brièvement dans le présent chapitre. Les propriétés thermodynamiques et les équilibres de phases ont été calculés à l'aide du logiciel thermochimique FactSage. En utilisant les paramètres de modèles obtenus pour les sous-systèmes binaires à ion commun, les sous-systèmes ternaires à cation commun (Na^+ ou K^+), et les sous-systèmes ternaires réciproques (avec Na^+ , K^+ , et deux anions) et en appliquant des techniques d'interpolation appropriées, nous avons pu effectuer des calculs dans le système multicomposant.

3.1 Modèle Quasichimique Modifié dans l'Approximation des Quadruplets (MQMQA)

Le liquide est une solution réciproque (avec plus d'un cation et plus d'un anion). Le MQMQA prend en compte la formation de quadruplets composés de deux cations et de deux anions par le biais d'un ordre à courte distance entre les ions premiers voisins (cation/anion, entre deux sous-réseaux) et les ions seconds voisins (cation/cation et anion/anion, dans un même sous-réseau), simultanément, suivant les réactions d'échange suivantes [45] :

$$(A-X-A) + (B-X-B) = 2(A-X-B); \Delta g_{AB/X_2} \quad (3.1)$$

$$(X-A-X) + (Y-A-Y) = 2(X-A-Y); \Delta g_{A_2/XY} \quad (3.2)$$

Où A et B sont deux cations différents (Na^+ et K^+ dans ce travail), et X et Y sont deux anions

différents. $\Delta g_{AB/X_2}$ et $\Delta g_{A_2/XY}$ sont des paramètres du modèle correspondant aux changements d'énergie de Gibbs pour les réactions d'échange de paires. Ils sont ajustés de façon à reproduire les données expérimentales disponibles dans les sous-systèmes binaires à anion commun A, B // X et à cation commun A // X, Y, respectivement.

Par exemple, dans le sous-système binaire à anion commun A, B // X, le paramètre $\Delta g_{AB/X_2}$ dépend des fractions molaires de paires X_{AA} et X_{BB} au lieu des fractions équivalentes, comme décrit ci-dessous [77]:

$$\Delta g_{AB/X_2} = \Delta g_{AB/X_2}^0 + \sum_{i \geq 1} g_{AB/X_2}^{i0} X_{AA}^i + \sum_{j \geq 1} g_{AB/X_2}^{0j} X_{BB}^j \quad (3.3)$$

$\Delta g_{AB/X_2}^0$, g_{AB/X_2}^{i0} et g_{AB/X_2}^{0j} sont les paramètres du modèle pouvant varier en fonction de la température. Dans les systèmes très ordonnés, les régions riches en AX et en BX peuvent être optimisées de manière presque indépendante. Cela signifie que l'optimisation de la région riche en AX n'aura pas d'impact significatif sur la région riche en BX, et vice versa.

Afin d'optimiser un sous-système ternaire réciproque A, B // X, Y, il est possible d'utiliser un paramètre d'interaction $\Delta g_{AB/XY}$ tel que décrit dans les chapitres 7 et 8. Ce paramètre correspond à la variation d'énergie de Gibbs pour former le quadruplet ABXY à partir des quadruplets binaires correspondants [45]:

$$\frac{1}{2} (ABX_2 + ABY_2 + A_2XY + B_2XY) = 2(ABXY) \quad (3.4)$$

Dans le MQMQA, les nombres de coordination seconds voisins varient en fonction de la composition dans la solution liquide. Prenons l'exemple d'un sous-système binaire A, B // X. Les nombres de coordination seconds voisins Z_A et Z_B des cations A et B sont indiqués ci-dessous [77]:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left(\frac{2 n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{AA} + n_{AB}} \right) \quad (3.5)$$

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left(\frac{2 n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{BA}^B} \left(\frac{n_{AB}}{2n_{BB} + n_{AB}} \right) \quad (3.6)$$

Z_{AA}^A et Z_{AB}^A sont les valeurs de Z_A lorsque tous les seconds voisins d'un cation A sont des A, et lorsque tous les seconds voisins d'un cation A sont des B. Z_{BB}^B et Z_{BA}^B sont définis de manière similaire. Le ratio (Z_{BA}^B / Z_{AB}^A) permet de fixer la composition d'ordonnement maximum dans le liquide. Dans le cas d'une solution solide (telle que hP22), les nombres de coordination sont nécessairement constants; ce qui implique que $Z_{AA}^A = Z_{AB}^A = Z_{BB}^B = Z_{BA}^B$.

Dans le cadre de notre modélisation thermodynamique, nous avons utilisé des modèles géométriques symétrique ou asymétrique pour estimer l'énergie de Gibbs en excès dans un système ternaire à cation commun (Na^+ ou K^+) (voir chapitres 7 et 8) à partir des paramètres optimisés pour les trois sous-systèmes binaires à cation commun. Il est possible d'utiliser des paramètres ternaires pour améliorer l'accord entre les calculs et les données expérimentales ternaires, si nécessaire. Ces paramètres ternaires expriment l'effet du troisième anion sur l'énergie de la paire formée par les deux autres anions.

Il existe deux types de modèles géométriques pour estimer l'énergie de Gibbs en excès dans un système ternaire à cation commun (Na^+ ou K^+ dans ce travail) : les modèles symétriques et les modèles asymétriques [78]. Les modèles symétriques, tels que ceux proposés par Kohler et Muggianu, considèrent que les trois composants se comportent de manière similaire. Dans ce travail, nous avons fait cette hypothèse pour tous les anions de même valence (CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , et $\text{Mo}_2\text{O}_7^{2-}$). Les modèles asymétriques, tels que ceux de Kohler-Toop et de Muggianu-Toop, prennent en compte le fait qu'un des trois composants a un comportement différent de celui des deux autres. Dans ce travail, nous avons introduit une asymétrie pour l'anion Cl^- , qui est le seul anion monovalent considéré.

Nous avons finalement utilisé deux méthodes d'interpolation différentes : la méthode symétrique de type Kohler (Figure 3.1) et la méthode asymétrique de type Kohler-Toop (Figure 3.2). Le calcul de l'énergie de Gibbs en excès pour une composition ternaire donnée p dépend du modèle géométrique choisi. Les propriétés des sous-systèmes binaires aux points a, b et c sont utilisées dans ce calcul, et les compositions binaires associées dépendent du modèle géométrique adopté.

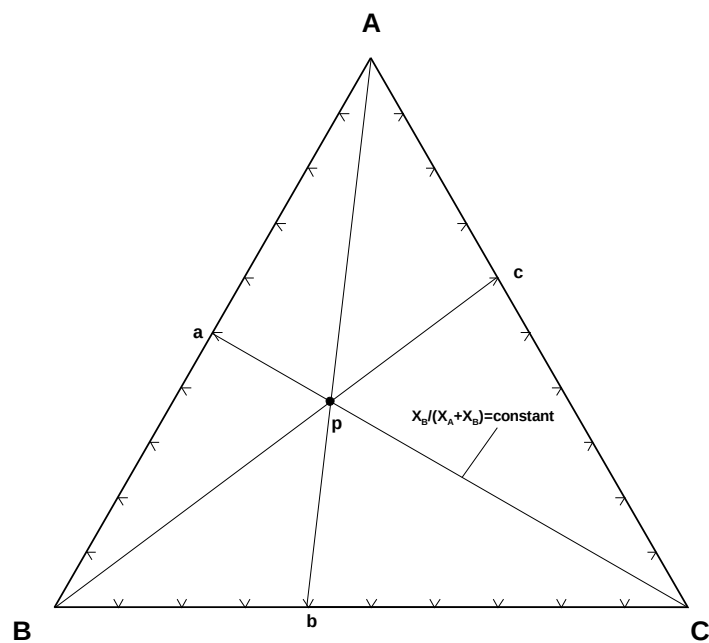


Figure 3.1 Méthode d'interpolation des paramètres binaires dans un système ternaire (modèle de Kohler) [78]

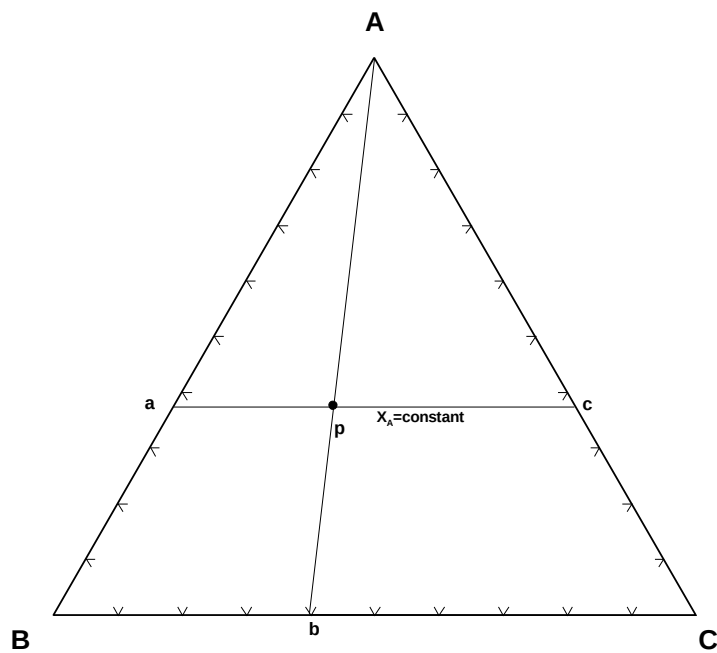


Figure 3.2 Méthode d'interpolation des paramètres binaires dans un système ternaire (modèle de Kohler-Toop) [78]

Les variables de composition suivantes χ_{12} sont utilisées pour étendre la notion de symétrie/asymétrie à un système multicomposant [78] :

$$\chi_{12} = \frac{\sum_{i=1,k} \sum_{j=1,k} X_{ij}}{\sum_{i=1,2,k,l} \sum_{j=1,2,k,l} X_{ij}} \quad (3.7)$$

Où k désigne toutes les valeurs de k dans les sous-systèmes ternaires asymétriques 1-2- k où 2 est le composant asymétrique, et l désigne toutes les valeurs de l dans les sous-systèmes ternaires asymétriques 1-2- l où 1 est le composant asymétrique.

La Figure 3.1 correspond à un système ternaire A-B-C symétrique pour lequel le paramètre Δg_{AB} a l'expression suivante [78] :

$$\Delta g_{AB} = \Delta g_{AB}^0 + \sum_{i \geq 1} g_{AB}^{i0} \left(\frac{X_{AA}}{X_{AA} + X_{AB} + X_{BB}} \right)^i + \sum_{j \geq 1} g_{AB}^{0j} \left(\frac{X_{BB}}{X_{AA} + X_{AB} + X_{BB}} \right)^j \quad (3.8)$$

La Figure 3.2 correspond à un système ternaire asymétrique, où le composant A est asymétrique. Le paramètre Δg_{AB} a alors l'expression suivante [78] :

$$\Delta g_{AB} = \Delta g_{AB}^0 + \sum_{i \geq 1} g_{AB}^{i0} X_{AA}^i + \sum_{j \geq 1} g_{AB}^{0j} (X_{BB} + X_{BC} + X_{CC})^j \quad (3.9)$$

3.2 « Compound Energy Formalism » (CEF)

A l'exception de la solution solide hexagonale hP22 (qui a été modélisée avec le MQMQA), nous avons utilisé le « Compound Energy Formalism » (CEF) [46, 48, 79] pour toutes les autres solutions solides (constituées de deux sous-réseaux ou plus). Le CEF peut par exemple être utilisé pour les solutions interstitielles et les composés non stœchiométriques. Le formalisme flexible décrit par Hillert [46] permet de représenter mathématiquement le comportement thermodynamique de différentes solutions solides. Dans notre travail (voir chapitres 7 et 8), nous avons donné deux exemples de solutions solides modélisées à l'aide du CEF.

De nombreuses solutions solides de sels inorganiques peuvent être décrites avec deux sous-réseaux distincts : un sous-réseau cationique où se distribuent les cations, et un sous-réseau anionique où se distribuent les anions.

Plus de deux sous-réseaux sont parfois nécessaires pour décrire correctement une solution solide. En effet, il pourrait y avoir plusieurs sites cristallins pour les cations, où certains cations préféreraient un site spécifique tandis que d'autres cations préféreraient un autre site [39]. Cette situation se produit par exemple pour la phase spinelle AB_2O_4 , qui nécessite trois sous-réseaux différents : le cation A^{2+} occupe principalement les sites tétraédriques, le cation B^{3+} a une préférence pour les sites octaédriques, et l'anion O^{2-} occupe le troisième sous-réseau [39].

CHAPITRE 4 OBJECTIFS DE LA RECHERCHE ET COHÉRENCE DES ARTICLES

Ce projet de recherche vise à parvenir à une meilleure compréhension des réactions impliquant les phases corrosives de chromates, dichromates, molybdates, dimolybdates, tungstates et ditungstates de sodium et de potassium à haute température (typiquement entre 600 et 950°C). Ces réactions corrosives se produisent principalement dans des environnements riches en H-O-S-C-Cl et en sels alcalins.

4.1 Question de recherche

L'ajout de chromates et dichromates (Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, et $\text{K}_2\text{Cr}_2\text{O}_7$), de molybdates et dimolybdates (Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, et $\text{K}_2\text{Mo}_2\text{O}_7$), de tungstates et ditungstates (Na_2WO_4 , K_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, et $\text{K}_2\text{W}_2\text{O}_7$) au modèle thermodynamique existant pour le système Na^+ , $\text{K}^+ \parallel \text{Cl}^-$, CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$ permettra-t-il à l'industrie et aux chercheurs de mieux comprendre les phénomènes réactionnels de corrosion et d'éviter en particulier la formation de phases liquides corrosives, à l'aide de calculs thermochimiques?

4.2 Objectifs de recherche

4.2.1 Objectifs principaux

- Développement d'un nouveau modèle thermodynamique pour prédire la nature et la composition des produits de corrosion liés aux éléments d'alliage Cr, Mo et W dans les aciers et les aciers inoxydables lors des procédés de conversion de l'énergie par combustion ;
- Développement d'équations d'énergie de Gibbs en fonction de la température et de la composition pour les différentes phases susceptibles de se former.

4.2.2 Objectifs secondaires

- Ajout des chromates et dichromates (Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, et $\text{K}_2\text{Cr}_2\text{O}_7$) au modèle thermodynamique existant pour le système Na^+ , $\text{K}^+ \parallel \text{Cl}^-$, CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$;

- Ajout des molybdates et dimolybdates (Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, et $\text{K}_2\text{Mo}_2\text{O}_7$) au système modélisé précédemment (Na^+ , $\text{K}^+ \parallel \text{Cl}^-$, CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, O^{2-}). Les constituants Na_2O et K_2O ont été ajoutés en quantités diluées dans la phase liquide de façon à pouvoir prendre en compte les réactions du type $2 \text{A}_2\text{MO}_4 = \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$, où $\text{A} = \text{Na}, \text{K}$ et $\text{M} = \text{Cr}, \text{Mo}$;
- Début de l'ajout des tungstates et ditungstates (Na_2WO_4 , K_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, et $\text{K}_2\text{W}_2\text{O}_7$) au système modélisé précédemment (Na^+ , $\text{K}^+ \parallel \text{Cl}^-$, CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, O^{2-}). **Malheureusement, il n'a pas été possible de terminer la modélisation thermodynamique de ce système dans le cadre de cette thèse ;**
- Planification de mesures expérimentales de DSC-TGA pour les composés purs A_2MO_4 (où $\text{A} = \text{Na}, \text{K}$ et $\text{M} = \text{Cr}, \text{Mo}, \text{W}$), pour plusieurs compositions binaires à ion commun, et pour 1 composition ternaire à cation commun (K^+) au centre de recherche Åbo Akademi Process Chemistry Centre (Turku, Finlande) afin de générer de nouvelles données permettant de mieux calibrer le modèle thermodynamique.

4.3 Présentation et cohérence des articles

Les objectifs assignés à cette recherche ont servi à structurer l'ensemble de ce document. Les chapitres 5, 6, 7 et 8 présentent les quatre articles soumis pour publication et constituant le corps principal de ce travail. Ces articles apportent des connaissances pertinentes et originales dans le domaine d'étude envisagé.

La première étape du développement de notre modèle thermodynamique a fait l'objet de deux articles scientifiques correspondants aux chapitres 5 et 6 de ce document, et soumis tous deux pour publication dans « Journal of Physical and Chemical Reference Data ». Une recherche bibliographique approfondie a été réalisée dans le cadre de cette étude sur les chromates et dichromates (Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, et $\text{K}_2\text{Cr}_2\text{O}_7$), les molybdates et dimolybdates (Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, et $\text{K}_2\text{Mo}_2\text{O}_7$), et les tungstates et ditungstates (Na_2WO_4 , K_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, et $\text{K}_2\text{W}_2\text{O}_7$) de sodium et de potassium. Nous avons ainsi évalué les structures cristallographiques et groupes d'espace de tous les allotropes des douze composés purs, ainsi que

leurs propriétés thermodynamiques ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$ et C_P). Il s'agissait d'identifier et de collecter tous les articles comportant des données expérimentales pouvant servir à la calibration de notre modèle thermodynamique. À partir des conditions expérimentales rapportées par les auteurs (technique expérimentale, pureté des réactifs, etc.), les données les plus fiables ont été identifiées. En parallèle, nous avons effectué des expériences de DSC-TGA pour mesurer les températures de transition solide-solide et de fusion pour les six composés purs A_2MO_4 (où $A = \text{Na}$ ou K , et $M = \text{Cr}$, Mo ou W) ainsi que les variations d'enthalpie correspondantes.

Le chapitre 7, correspondant au troisième article, a été soumis pour publication dans « Chemical Engineering Science ». Il est consacré à la modélisation thermodynamique du système de sels à base de chromates et dichromates de sodium et de potassium suivant : ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{O}$) (dilué en oxydes libres).

L'approche de type CALPHAD a été adoptée. La phase liquide et la solution solide hexagonale hP22 de haute température ont été modélisées avec le MQMQA, tandis que le CEF a été utilisé pour modéliser toutes les autres solutions solides.

Les données de diagrammes de phases les plus fiables issues de la littérature et les données issues de nos mesures de DSC-TGA ont été utilisées pour la modélisation des sous-systèmes binaires à ion commun et d'ordre supérieur.

Le chapitre 8, correspondant au quatrième article, a été soumis pour publication dans « Industrial & Engineering Chemistry Research ». La même stratégie que précédemment a été employée pour la modélisation des sous-systèmes binaires à ion commun et d'ordre supérieur à base de molybdates et de dimolybdates de sodium et de potassium pour le système de sel ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) (dilué en oxydes libres).

4.4 Pertinence et contributions originales

La pertinence et les contributions originales de ce projet à la communauté scientifique résident dans le développement d'un nouveau modèle thermodynamique pertinent pour de nombreux

procédés industriels évoqués auparavant, en particulier lors de la conversion d'énergie par combustion. Ce modèle thermodynamique incluant les chromates, dichromates, molybdates et dimolybdates de sodium et de potassium devrait permettre d'acquérir une meilleure compréhension des phénomènes de corrosion « catastrophique » et plus particulièrement d'éviter la formation d'une phase liquide corrosive.

La capacité prédictive du modèle développé permettra, à l'aide de calculs avec le logiciel thermochimique FactSage, d'optimiser les paramètres d'exploitation et d'améliorer les performances énergétiques de nombreux procédés industriels; d'où une réduction significative du temps et de l'argent investis dans des mesures expérimentales faites en laboratoire.

CHAPITRE 5 ARTICLE 1 : CRITICAL EVALUATION AND CALORIMETRIC STUDY OF THE THERMODYNAMIC PROPERTIES OF Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 , AND K_2WO_4

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Submitted for publication in Journal of Physical and Chemical Reference Data on April 14, 2023

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

5.1 Introduction

Installations producing energy by combustion suffer from the problem of hot corrosion, which limits their efficiency [19, 20, 26, 36]. This phenomenon is an accelerated form of oxidation (from 600 to 950°C) [14, 57] affecting equipment in the presence of high-temperature combustion gases (N_2 , CO_2 , CO , O_2 , H_2O , etc.) containing impurities (SO_2 , Cl_2 , S_2 , HCl , etc.) and corrosive products (Na_2O , K_2O , NaOH , KOH , NaCl , KCl , etc.) [20, 26, 35]. The formation of ashes and corrosive

gases is mainly due to the elements K, Na, Ca, Mg, Fe, Al, Si, P, S, Cl, C, H, and O [24, 25]. Stainless steels containing the alloying elements Ni, Cr, Mo, W, and V are particularly prone to this problem [19-23]. They are frequently exposed to gaseous species generated during combustion (O_2 , CO_2 , SO_2 , H_2O) or from the evaporation of ashes (KCl, NaCl, Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3) [14, 20, 26, 27].

Oxides formed from these alloying elements, such as Cr_2O_3 [21, 29], MoO_3 , WO_3 , and V_2O_5 [21, 23, 36], often react with the KCl, NaCl, Na_2SO_4 , K_2SO_4 , Na_2CO_3 , and K_2CO_3 present during the operating conditions of these installations and/or originating from the fuel used. Those along with the quantity of air required for combustion contribute to the oxidation of the alloying elements. The literature reports that, under operating conditions, corrosive deposits in the form of Na_2CrO_4 and K_2CrO_4 [29, 30] may be formed on the walls of installations. Other salts can further enhance the corrosion, particularly sodium molybdate [30, 32], potassium molybdate, sodium tungstate [30, 33], and potassium tungstate. These may be present in solid or liquid form.

Studies by Misra [22] and Fryberg [32] revealed the complete conversion of Na_2SO_4 to Na_2CrO_4 before the onset of catastrophic corrosion for Mo-containing superalloys. Initiation of catastrophic corrosion was characterized by the conversion of Na_2CrO_4 to Na_2MoO_4 observed in the MoO_3 -rich layer at the scale-metal interface, related to fluxing by the Na_2MoO_4 - MoO_3 mixture.

Catastrophic corrosion is attributable to the formation of Na_2MoO_4 and a Na_2MoO_4 - MoO_3 mixture, but its mechanisms are still unclear. The presence of sodium in the MoO_3 - WO_3 zones reduces the melting temperature by forming Na_2MoO_4 - Na_2WO_4 [32]. Furthermore, Bourhis and Saint-John [80] reported catastrophic corrosion in Mo-containing superalloys related to fluxing by MoO_3 , which forms at the scale-metal interface.

In this context, predicting potential corrosion products to ensure the preservation of equipment while maximizing the rate of conversion into electrical energy is extremely important. Indeed, the various deposits, rich in salts, are generally very corrosive and, when present in liquid form, often dissolve the protective oxide layers and attack the metal surface [74].

A thermodynamic model for the Na^+ , $K^+ // Cl^-$, SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $Cr_2O_7^{2-}$, MoO_4^{2-} , $Mo_2O_7^{2-}$, WO_4^{2-} , $W_2O_7^{2-}$, O^{2-} system is being developed. This will permit us to make phase equilibrium

calculations, and thus assess the limiting conditions under which deposits are susceptible to form and then prevent their formation. As a first step, it is necessary to investigate the crystal structures and thermodynamic properties (including solid-solid transition and fusion) of all relevant pure salts. The present article is devoted to a thorough literature review for the sodium and potassium chromates, molybdates, and tungstates. The sodium and potassium dichromates, dimolybdates and ditungstates will be discussed in a subsequent paper. For the six compounds considered in this work, literature data are sometimes lacking or contradictory. Therefore, differential scanning calorimetry (DSC) was used to measure the temperature and enthalpy change for the solid-solid transitions and fusion of the various compounds investigated. In addition, high temperature X-ray diffraction (XRD) measurements were conducted for K_2MoO_4 .

5.2 Experimental procedure

5.2.1 DSC/TGA (differential scanning calorimetry/thermogravimetric analysis)

Materials and measurements

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

Chemical formula	Supplier	CAS number	Purity (%)
$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$	Sigma-Aldrich	10034-82-9	99.0
K_2CrO_4	Alfa-Aesar	7789-00-6	99.9
Na_2MoO_4	Sigma-Aldrich	7631-95-0	99.9
K_2MoO_4	Sigma-Aldrich	13446-49-6	98

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	Sigma-Aldrich	10213-10-2	99.995
K_2WO_4	Alfa-Aesar	7790-60-5	99.5

DSC/TGA (differential scanning calorimetry/thermogravimetric analysis) experiments were conducted to measure the temperature and enthalpy change for the solid-solid transitions and fusion of the pure compounds Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 , and K_2WO_4 . These measurements were performed using a NETZSCH STA 449 F1 Jupiter® simultaneous DSC-TGA equipment.

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

BaCO_3 (purity of 99.98%) with $T_{\text{trans}} (\text{S1-S2}) = 808^\circ\text{C}$;

CsCl (purity of 99.99%) with $T_{\text{trans}} (\text{S1-S2}) = 476^\circ\text{C}$;

Ag_2SO_4 (purity of 99.999%) with $T_{\text{trans}} (\text{S1-S2}) = 426^\circ\text{C}$;

and $\text{C}_6\text{H}_5\text{COOH}$ (purity of 99.5%) with $T_{\text{trans}} (\text{S-L}) = 122^\circ\text{C}$.

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

A dehydration treatment of all pure compounds was performed prior to the DSC measurements. This operation was performed in a Vulcan oven temperature (Model: 3-130) to eliminate water absorbed by the samples during their storage, and also most of the water present in the initial reagents $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. All reagents were heated for 3 hours at 200°C and then cooled to 25°C .

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

Initial heating was performed from room temperature to 40°C , followed by a 10 min isothermal hold to ensure thermal stability of the sample and reference. Three consecutive heating-cooling

cycles were then conducted for each sample, with a heating/cooling rate of 10°C/min.

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

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

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

Setting up the baseline

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

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

5.2.2 High temperature X-ray diffraction

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

The powder was ground in an agate mortar to $\sim 50\ \mu\text{m}$ particle size to ensure cohesion and then spread evenly on a flat sample holder. The used XRD device was X'Pert Pro MPD Powder model (by Malvern Panalytical), which was connected to a high-temperature chamber Anton Paar HTK 1200N and temperature controller TCU1000N. This setup enabled autonomous temperature control and diffraction measurements. Tube gave $\text{CuK}\alpha$ radiation and was set at 40 kV and 40 mA.

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

5.3 Crystal structures and space groups

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

Crystal structure information for $\text{Na}_2\text{CrO}_{4(\text{S1},\text{S2})}$ and $\text{K}_2\text{CrO}_{4(\text{S1},\text{S2})}$ is summarized in Tables 5.1 and 5.2 respectively.

Table 5.1 Crystallographic data for polymorphs of Na_2CrO_4

Allotrope of Na_2CrO_4	Crystal structure	Space group	Reference
$\text{Na}_2\text{CrO}_{4(\text{S1})}$	Orthorhombic (stable below 420°C)	D_{2h}^6 -Pbnn	[81]
		Cmcm	[82]
			[83]

			[84]
			[85]
			[86]
Na_2CrO_4 (S2)	Hexagonal (stable from 420 to 790°C)	$\text{P6}_3\text{mc}$	[84]
		$\text{P6}_3/\text{mmc}$	[87]

Table 5.2 Crystallographic data for polymorphs of K_2CrO_4

Allotrope of K_2CrO_4	Crystal structure	Space group	Reference
K_2CrO_4 (S1)	Orthorhombic (stable below 669°C)	Pcmn	[84]
		Pnam	[88]
		-	[89]
K_2CrO_4 (S2)	Hexagonal (stable from 669 to 976°C)	$\text{P6}_3\text{mc}$	[84]
		$\text{P6}/\text{mmc}$, P6mc , $\text{P}\bar{6}2\text{c}$, $\text{P}\bar{3}1\text{c}$, P31c	[88]

Miller's [81] visual estimation in single-crystal X-ray oscillation intensities showed that Na_2CrO_4 (S1) (low-temperature allotrope) is orthorhombic with D_{2h}^6 -Pbnn space group. This study was subsequently reviewed by Fischmeister [82], Niggli [83], Goldberg [84], Nimmo [85], and Amirthalingam [86] who confirmed a different space group, Cmcm.

The crystal structure of K_2CrO_4 (S1) at room temperature has been investigated by XRD [84, 87, 88]. An orthorhombic structure has been reported with space group Pnam [87, 88] or Pcmn [84].

The high-temperature allotropes Na_2CrO_4 (S2) and K_2CrO_4 (S2) exhibit hexagonal structures. The

analysis of high-temperature XRD diffractograms of A_2BX_4 -type compounds suggests the space group $P6_3mc$ for both allotropes with the presence of c-glide [90]; the two structures are isostructural with that of α - Ca_2SiO_4 [84]. For $Na_2CrO_{4(S2)}$, Ferrante [87] reported the space group $P6/mmc$. The XRD analysis of Pistorius [88] suggested that $K_2CrO_{4(S2)}$ has the same space group as K_2SO_4 : $P6/mmc$, $P6mc$, $P\bar{6}2C$, $P\bar{3}1C$, or $P31c$.

Crystal structure information for $Na_2MoO_{4(S1,S2,S3,S4)}$ is summarized in Table 5.3.

Table 5.3 Crystallographic data for polymorphs of Na_2MoO_4

Allotrope of Na_2MoO_4	Crystal structure	Space group	Reference
$Na_2MoO_{4(S1)}$	Cubic (stable below 457°C)	-	[91]
		Fd3m	[92]
		-	[93]
		$Fd\bar{3}m$	[94]
			[95]
			[96]
$Na_2MoO_{4(S2)}$	Orthorhombic (stable from 457 to 589°C)	-	[93]
		$Pbn2_1$	Reference 10 in [97]
$Na_2MoO_{4(S3)}$	Orthorhombic (stable from 589 to 641°C)	-	[93]
		Fddd	Reference 10 in [97]
			[95]
$Na_2MoO_{4(S4)}$	Hexagonal	$P6_3/mmc$	Reference 10 in [97]

	(stable from 641 to 687°C)		[95]
		-	[93]

The structure of the low-temperature allotrope (S_1) of Na_2MoO_4 is a spinel according to Lindqvist [91], with cubic crystal structure [91-96]. X-ray diffraction revealed the $\text{Fd}\bar{3}\text{m}$ space group [95], and further studies by Raman spectroscopy [94] and neutron powder diffraction [96] yielded the same space group. Swanson [92] reported the $\text{Fd}3\text{m}$ space group.

XRD patterns showed that the second allotrope (S_2) of Na_2MoO_4 is orthorhombic [93, 97] with space group $\text{Pbn}2_1$ [97]. Transition from S_2 to S_3 yielded the same crystal structure [93, 95, 97] with the Fddd space group [95, 97]. The high-temperature allotrope S_4 is hexagonal [93, 95, 97] with space group $\text{P}6_3/\text{mmc}$ [95, 97].

Crystal structure information for $\text{K}_2\text{MoO}_{4(S_1, S_2, S_3)}$ is summarized in Table 5.4.

Table 5.4 Crystallographic data for polymorphs of K_2MoO_4

Allotrope of K_2MoO_4	Crystal structure	Space group	Reference
$\text{K}_2\text{MoO}_{4(S_1)}$	Monoclinic (stable below 324°C)	C2/m	This work
			[98]
			[99]
		-	[100]
		C2/m	[101]
$\text{K}_2\text{MoO}_{4(S_2)}$	Orthorhombic (stable from 324 to 455°C)	Ccmm	This work
		-	[100]
		Ccmm	[102]

$K_2MoO_{4(S3)}$	Trigonal (stable from 455 to 928°C)	$P\bar{3}m1$	This work
		-	[100]
		$P\bar{3}m1$	[103]

K_2MoO_4 exhibits three allotropes. The low-temperature form S_1 is monoclinic. Our XRD analysis, the measurements of [98] (who performed three-dimensional Patterson and Fourier syntheses that were refined by least squares techniques) and those of [99-101] confirmed $C2/m$ as the space group. Our high-temperature XRD analysis showed that S_2 is orthorhombic, in agreement with [101, 102]. The space group identified by us ($Ccmm$) agrees with that reported by Berg et al. [102].

S_3 has also been studied by us using high-temperature XRD up to 500°C; analysis of the diffractogram indicated a trigonal structure. Akker et al. [103] erroneously reported an hexagonal structure. According to our results, the space group is $P\bar{3}m1$, in agreement with Akker et al [103].

According to Warczewski [100], transition from the intermediate-temperature polymorph S_2 to the high-temperature pseudohexagonal allotrope S_3 involves two modulated intermediate structures (incommensurable), which are orthorhombic and pseudohexagonal, respectively. Based on these data, K_2MoO_4 exhibits four allotropes, and the high-temperature form (S_4) is hexagonal. However, as will be explained later, this fourth allotrope was not observed in our high-temperature XRD analysis (at 465 and 500°C). Therefore, only three allotropes were considered for K_2MoO_4 in the present work.

Crystal structure information for $Na_2WO_{4(S1,S2,S3)}$ is summarized in Table 5.5.

Table 5.5 Crystallographic data for polymorphs of Na_2WO_4

Allotrope of Na_2WO_4	Crystal structure	Space group	Reference
$Na_2WO_{4(S1)}$	Cubic (stable below 588°C)	Fd3m	[104]
			[105]

		Fd $\bar{3}$ m	[94]
			[96]
			[106]
Na ₂ WO _{4(S2)}	Tetragonal (tentative) (stable from 588 to 589°C)	I41/amd (tentative)	[106]
Na ₂ WO _{4(S3)}	Orthorhombic (stable from 589 to 694°C)	Pnam – D_{2h}^{16}	[104]
		Fddd	[106]

There are some uncertainties in the literature regarding the number of allotropes for Na₂WO₄, as well as their crystal structures and space groups [94, 97, 104, 107-109]. XRD analyses conducted by Pistorius [104] and Temperature-Programmed X-ray powder Diffraction by Hämmer and Höppe [106] suggested the presence of three allotropes. However, the XRD analyses performed by Pistorius [104] have only identified with certainty two allotropes (S₁ and S₃). For Na₂WO_{4(S2)}, the diffraction pattern was of rather poor quality.

XRD analysis [110], Raman spectroscopy [94] and neutron diffraction [96] confirmed that the low-temperature allotrope Na₂WO_{4(S1)} is cubic with Fd $\bar{3}$ m space group. At room temperature, only Na₂MoO₄ and Na₂WO₄ exhibit an ordinary spinel structure among alkali metal sulfates, chromates, molybdates and tungstates [91, 96]. The work of Hämmer and Höppe [106] was the only one able to characterize the S₂ allotrope using Temperature-Programmed X-ray powder Diffraction (TPXRD); Austin and Pierce [108] had indicated that both solid-solid transitions were displaced and non-reconstructive. Therefore, obtaining single crystals of the high-temperature polymorphs of Na₂WO₄ by quenching was impossible, as well as the use of Rietveld refinement and differential scanning calorimetry. Based on TPXRD data, it is suggested that Na₂WO_{4(S2)} has a tetragonal unit

cell with lattice parameters $a = 1707.2$ pm, $c = 1293.6$ pm, and a space group consistent with symmetry relationships to $\text{Na}_2\text{WO}_{4(\text{S}1)}$, i.e. $I41/\text{amd}$ [106]. The latter is assumed to be a maximal subgroup of $\text{Fd}\bar{3}\text{m}$ and a direct supergroup of Fddd (space group of the allotrope S_3) [106]. Even with indexing and Pawley fitting ($R_{\text{Bragg}} = 0.013$, $R_{\text{wp}} = 0.058$), the structure of S_2 was not reliably determined. Thus, $\text{Na}_2\text{WO}_{4(\text{S}2)}$ was assumed to crystallize in the $I41/\text{amd}$ space group, with no symmetry relationship derivable between $\text{Na}_2\text{WO}_{4(\text{S}1)}$ and $\text{Na}_2\text{WO}_{4(\text{S}3)}$, and no proposed unit cell fitting into such a structure [106].

Very limited high-temperature XRD studies have been conducted to identify the structure and space group of the S_3 allotrope; Pistorius [104] and Hämmer and Höppe [106] reported an orthorhombic structure with different space groups (Pnam and Fddd , respectively).

Crystal structure information for $\text{K}_2\text{WO}_{4(\text{S}1,\text{S}2,\text{S}3)}$ is summarized in Table 5.6.

Table 5.6 Crystallographic data for polymorphs of K_2WO_4

Allotrope of K_2WO_4	Crystal structure	Space group	Reference
$\text{K}_2\text{WO}_{4(\text{S}1)}$	Monoclinic (stable below 368°C)	-	[111]
		$\text{C}2/\text{m}$	[103]
		-	[100]
$\text{K}_2\text{WO}_{4(\text{S}2)}$	Orthorhombic ($\beta\text{-K}_2\text{SO}_4$ type) (stable from 368 to 458°C)	-	[103]
$\text{K}_2\text{WO}_{4(\text{S}3)}$	Trigonal (stable from 458 to 926°C)	$\text{P}\bar{3}\text{m}1$	[103]
		-	[100]

K_2WO_4 displays three allotropes. The crystal structure was studied at room temperature by Raman spectroscopy [111] and XRD [100, 103], and was found to be monoclinic with $\text{C}2/\text{m}$ space group

[103]. The allotrope S_2 was examined by XRD only by Van Den Akker et al. [103], who suggested a β - K_2SO_4 type structure. However, the structure has not been reliably identified, and these authors indicated that most potassium salt phases have an orthorhombic structure (β - K_2SO_4 type).

For the S_3 allotrope, the XRD analyses of Warczewski [100] and Van Den Akker et al. [103] revealed a trigonal structure with $P\bar{3}m1$ space group [103]. Note that [100] and [103] incorrectly reported a hexagonal structure.

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

5.4.1 Sodium chromate

5.4.1.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transition for Na_2CrO_4

To measure the temperature and enthalpy change for the solid-solid transition of Na_2CrO_4 , DSC measurements were conducted in this work. In addition, data acquired by various experimental techniques were collected from the literature and are shown in Table 5.7.

Table 5.7 Temperature and enthalpy change of solid-solid transition for Na_2CrO_4

$T_{trans} \ S_1 \rightarrow S_2$ (°C)	$\Delta H_{trans} \ S_1 \rightarrow S_2$ (kJ/mol)	Experimental Method	Reference
417.3	8.487	DSC (2 nd heating) 10°C/min	This work
417.6	8.270	DSC (3 rd heating) 10°C/min	This work
413	-	Cooling curves	[112]
421 ± 4	-	DTA*	[113]

420	10.042	DTA	[114]
420.9 ± 3	9.581 ± 0.418	Drop calorimetry in an ice calorimeter	[115]
419	8.870	DTA	[84]
427	9.468	Drop calorimetry	[87]
419.4	10.061 (cooling) 9.599 (heating)	DSC 10°C/min	[116]
419.5	9.296	Weighted average of available data	This work

* The purity of salt is 99.5%

5.4.1.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for Na_2CrO_4

The thermodynamic properties of fusion (temperature and enthalpy change) were measured by [87, 112, 114, 115, 117-125]. The heat of fusion was obtained by drop calorimetry [87, 115] and DTA [114]. In this work, DSC measurements were conducted. As an example, the DSC thermogram (2nd and 3rd heating/cooling cycles only) for Na_2CrO_4 is shown in Figure 5.1. The DSC thermograms for all other compounds are presented in the Supporting Information (Appendix B). All data collected from the literature and obtained in the present work are presented in Table 5.8.

Table 5.8 Temperature and enthalpy of fusion for Na_2CrO_4

$T_f \text{ } S_2 \rightarrow L \text{ (}^\circ\text{C)}$	$\Delta H_f \text{ } S_2 \rightarrow L \text{ (kJ/mol)}$	Experimental Method	Reference
783	18.481	DSC (2 nd heating) 10°C/min	This work
783.4	19.599	DSC (3 rd heating)	This work

		10°C/min	
792	-	Cooling curves	[112]
780	-	Visual observation with a Pt/Pt-Rh thermocouple	[117]
794.5	-	Cooling curves	[118]
792	-	Calibrated thermocouple with recorder potentiometer	[119]
791.9	-	DTA	[120]
793	-	Visual observation with a Pt/Pt-Rh thermocouple	[121]
796	25.146	DTA	[114]
792.4 ± 1	-	DTA and high-temperature microscopy	[122]
794	-	Visual-polythermal method	[123]
796.9 ± 2	24.225 ± 0.418	Drop calorimetry in an ice calorimeter	[115]
792	24.309	Drop calorimetry*	[87]
785.6	-	DTA	[124]
795.1	-	DTA	[125]
790.2	23.220	Weighted average of available data	This work

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

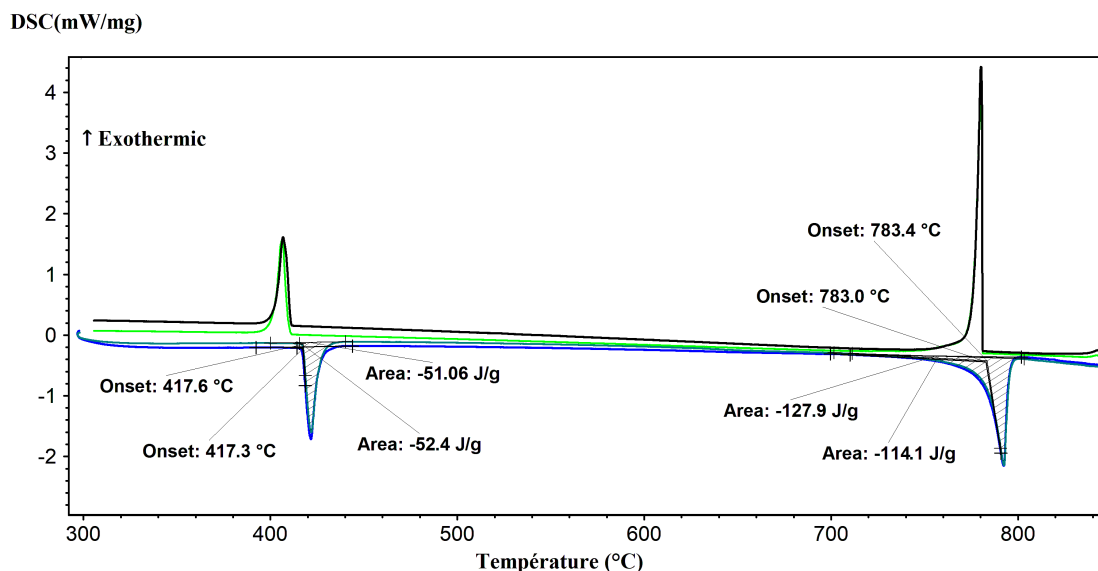


Figure 5.1 Differential scanning calorimetry (DSC) thermogram for Na_2CrO_4 (2nd and 3rd heating/cooling cycles only)

5.4.1.3 Recommended thermodynamic data for sodium chromate Na_2CrO_4

Our selected thermodynamic data ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_P) for sodium chromate (Na_2CrO_4) are provided in Table 5.9. For the pure liquid, below the temperature of fusion, the heat capacity (as a function of temperature) over a given temperature range was taken identical to that of the solid phase stable over this specific temperature range (i.e. C_P of the low-temperature allotrope (S_1) between 298.15 and 692.1 K, and C_P of the high-temperature allotrope (S_2) between 692.1 and 1063.4 K). Similarly, for solid (S_2), below the temperature of the solid-solid transition, the heat capacity was taken identical to that of solid (S_1). For all three phases, the heat capacity above the maximum temperature T_{max} of the highest temperature range in Table 5.9 is assumed to be constant and equal to the value of C_P at T_{max} .

The same approach was used for all other compounds considered in this work, even when there were more than two allotropes. More details on the thermodynamic properties selected for Na_2CrO_4 are given below.

Table 5.9 Selected thermodynamic properties of Na₂CrO₄

Compound	T Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol) ^a	$S_{298.15\text{ K}}^\circ$ (J/mol.K) ^b	C_p (J/mol.K)
Na ₂ CrO _{4(s1)}	298.15 to 692.1 (This work)	-1 341 491.5 (This work)	176.6150 [87]	101.0687 + 0.13999664T/K [115]
Na ₂ CrO _{4(s2)}	298.15 to 692.1 692.1 to 1063.4 (This work)	-1 332 195.5 (This work)	190.0467 (This work)	101.0687 + 0.13999664T/K [115] 149.9420 + 0.05159709T/K [115]
Na ₂ CrO _{4(l)}	298.15 to 692.1 692.1 to 1063.4 1063.4 to 2000 (This work)	-1 308 975.0 (This work)	211.8827 (This work)	101.0687 + 0.13999664T/K [115] 149.9420 + 0.05159709T/K [115] 204.7775 [115]

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

^b Absolute (third law) entropy.

The data presented in Table 5.7 and Table 5.8 are in good agreement. Our selected values of the temperatures for the solid-solid transition and fusion of Na₂CrO₄ are the weighted average of all data found in the literature as well as our two DSC measurements (2nd and 3rd heating runs shown in Figure 5.1); the weighting was based on the expected accuracy of each experimental technique. The same methodology was applied for our selected values of the enthalpy changes for Na₂CrO₄. A similar approach was used for all other compounds investigated in this work.

The value of the standard enthalpy at 298.15 K ($\Delta H_{298.15\text{ K}}^\circ$) for Na₂CrO_{4(s1)} was estimated as follows. The enthalpy of dissolution in water of Na₂CrO_{4(s1)} ($\text{Na}_2\text{CrO}_{4(s1)} \rightarrow 2\text{Na}_{(\text{aq})}^+ + \text{CrO}_{4(\text{aq})}^{2-}$) was measured by calorimetry [126] as -19,120.9 J/mol. According to the most recent databases of the FactSage software package [42], $\Delta H_{298.15\text{ K}}^\circ(\text{Na}_{(\text{aq})}^+) = -239,731\text{ J/mol}$ and $\Delta H_{298.15\text{ K}}^\circ(\text{CrO}_{4(\text{aq})}^{2-}) = -881,150.4\text{ J/mol}$. The obtained value of -1,341,491.5 J/mol for $\Delta H_{298.15\text{ K}}^\circ(\text{Na}_2\text{CrO}_{4(s1)})$ is very close to that of -1,342,198 J/mol recommended in Barin's

compilation [127]. The Open Quantum Materials Database (OQMD) [128, 129] reported an enthalpy of formation at 0 K of -1,331,208 J/mol derived from Density Functional Theory (DFT) calculations. The corresponding value given in Materials Project [130] is -1,343,365 J/mol.

The standard entropy at 298.15 K ($S_{298.15\text{ K}}^\circ$) of $\text{Na}_2\text{CrO}_{4(\text{S1})}$ was derived by Ferrante et al. [87] as 176.6150 J/mol.K by integration of their experimental C_p values from 5.5 to 308.5 K using adiabatic calorimetry. This value is identical to that recommended in Barin's compilation (176.611 J/mol.K) [127].

To our knowledge, no other direct heat capacity measurements are available for Na_2CrO_4 . Denielou et al. [115] carried out heat content measurements using drop calorimetry in an ice calorimeter. The salts were then analyzed using XRD to confirm that they were in their stable form. Enthalpy variations $H_T - H_{273.15\text{ K}}$ as a function of temperature were obtained as follows. For $\text{Na}_2\text{CrO}_{4(\text{S1})}$, nine measurements were performed between 370 and 665 K, and the following fit was provided by Denielou et al. : $H_T - H_{273.15\text{ K}} = 1.673 \times 10^{-2} T^2 + 24.156 T - 7,835$ cal/mol (0.4%, empirical standard deviation of 6 calories) [115]. For $\text{Na}_2\text{CrO}_{4(\text{S2})}$, eleven measurements were conducted between 698 and 1065 K, with the following fit : $H_T - H_{273.15\text{ K}} = 6.166 \times 10^{-3} T^2 + 35.837 T - 8,566$ cal/mol (0.15%, empirical standard deviation of 7 calories) [115]. Finally, for $\text{Na}_2\text{CrO}_{4(\text{L})}$, at least eleven measurements were made above 1091 K, with the following fit : $H_T - H_{273.15\text{ K}} = 48.943 T - 9,737$ cal/mol (0.11%, empirical standard deviation of 12 calories) [115].

For each phase of Na_2CrO_4 , the heat capacity expression (as a function of temperature) was derived by us from the fits of $H_T - H_{273.15\text{ K}}$ provided by Denielou et al. [115]. Calculated values of $H_T - H_{298.15\text{ K}}$ are compared to the available data in Figure 5.2. This figure includes the heat contents $H_T - H_{298.15\text{ K}}$ measured by Ferrante et al. [87] as well as the $H_T - H_{298.15\text{ K}}$ values obtained by conversion of the $H_T - H_{273.15\text{ K}}$ data of Denielou et al. [115] [$H_T - H_{298.15\text{ K}} = (H_T - H_{273.15\text{ K}}) - (H_{298.15\text{ K}} - H_{273.15\text{ K}})$]. These two series of data are in good agreement.

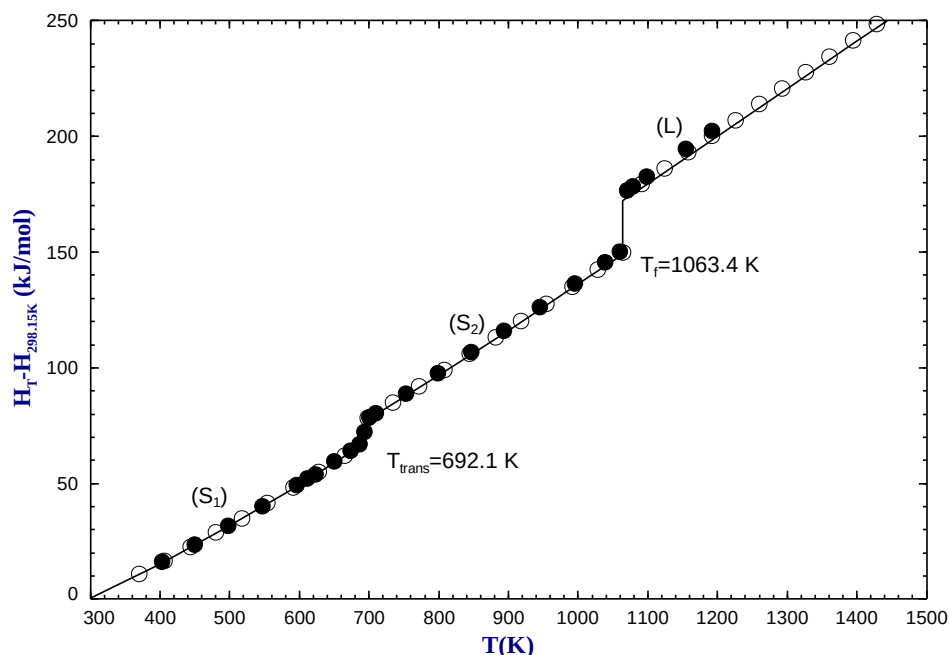


Figure 5.2 Calculated heat content $H_T - H_{298.15\text{ K}}$ for Na_2CrO_4 (enthalpies of transition are the weighted average of all available data presented in Tables 5.7 and 5.8). Experimental data from [87] (●) and [115] (○).

5.4.2 Potassium chromate

5.4.2.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transition for K_2CrO_4

The temperature and enthalpy change for the solid-solid transition of K_2CrO_4 was measured by DSC in the present work. These data along with all measurements collected from the literature (and obtained using various experimental techniques) are gathered in Table 5.10. Our experimental DSC thermogram is provided in the Supporting Information (Figure B1).

Table 5.10 Temperature and enthalpy change of solid-solid transition for K_2CrO_4

$T_{\text{trans}} \text{ } S_1 \rightarrow S_2 \text{ (}^\circ\text{C)}$	$\Delta H_{\text{trans}} \text{ } S_1 \rightarrow S_2 \text{ (kJ/mol)}$	Experimental Method	Reference
670.7	7.201	DSC (2 nd heating) 10°C/min	This work
671.2	7.123	DSC (3 rd heating) 10°C/min	This work
666	-	Heating or cooling curves	[131]
679*	-	Pyrometry	[132]
669	-	Cooling curves	[112]
666	-	Cooling curves with visual reading	[133]
664	10.251	Heating or cooling curves	[134]
666.8	-	Thermocouple Pt-Rh	[135]
669	-	Cooling curves	[136]
663	-	Resistance technique	[88]
671	7.155	DTA	[114]
665	10.2	-	[137]
668.5 ± 3	-	DTA (the purity of this salt is 99.8%)	[138]
675	-	DTA (the purity of this salt is 99.96%)	[139]

662.9 ± 3	9.954 ± 0.502	Enthalpimetric analysis using an ice calorimeter	[140]
674 [DTA and DSC]	6.583 [DSC] 5.243 [DTA]	DTA and DSC (the purity of this salt is 99.87%) 5°C/min	[141]
670.2 ± 3	7.2 ± 0.25 6.908 [questionable according to the authors]	DSC 10°C/min (heating) 40°C/min (cooling)	[142]
668.9	-	Electrical Conductivity of Single Crystals	[143]
669.2	8.390	Weighted average of available data	This work

* This temperature was discarded since it is significantly higher than all other temperatures reported in the literature.

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

The temperature and enthalpy of fusion have been measured by [112, 114, 120, 122, 131-133, 135, 137, 140, 144-148] . The heat of fusion was obtained by enthalpimetric analysis [140] and DTA [114] . All data from the literature and our DSC measurements are given in Table 5.11.

Table 5.11 Temperature and enthalpy of fusion for K_2CrO_4

T_f $S_2 \rightarrow L$ (°C)	ΔH_f $S_2 \rightarrow L$ (kJ/mol)	Experimental Method	Reference
977.2	32.896	DSC (2 nd heating) 10°C/min	This work
976.4	34.197	DSC (3 rd heating)	This work

		10°C/min	
971	-	Heating or cooling curves	[131]
984	-	Pyrometry	[132]
976	-	Cooling curves	[112]
978	-	Cooling curves with visual reading	[133]
968.3	-	Thermocouple Pt-Rh	[135]
970.9	-	Cooling curves	[144]
976	-	DTA	[120]
972	-	Visual-polythermal method	[145]
979	31.547	DTA	[114]
984	28.9	-	[137]
980	-	DTA and high-temperature microscopy	[122]
984	-	DTA	[146]
976	-	Visual-polythermal method	[147]
968	-	Visual observation with a Pt/Pt-Rh thermocouple	[148]
973.9 ± 4	32.991 ± 0.669	Enthalpimetric analysis using an ice calorimeter	[140]
975.8	32.925	Weighted average of available data	This work

5.4.2.3 Recommended thermodynamic data for potassium chromate K_2CrO_4

Our selected thermodynamic data ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_p) for potassium chromate (K_2CrO_4) are given in Table 5.12.

Table 5.12 Selected thermodynamic properties of K_2CrO_4

Compound	T Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol)	$S_{298.15\text{ K}}^\circ$ (J/mol.K)	C_p (J/mol.K)
$K_2CrO_{4(S1)}$	298.15 to 942.4 (This work)	-1 403 700.0 [149]	199.9952 [150]	$144.275 + 0.0611905T/K$ [140]
$K_2CrO_{4(S2)}$	298.15 to 942.4 942.4 to 1249 (This work) 1249 to 2000* (This work)	-1 395 309.6 (This work)	208.8984 (This work)	$144.275 + 0.0611905T/K$ [140] $44.89432 + 0.15338544T/K$ [140] 212.007464
$K_2CrO_{4(L)}$	298.15 to 942.4 942.4 to 1249 1249 to 2000 (This work)	-1 362 385.1 (This work)	235.2591 (This work)	$144.275 + 0.0611905T/K$ [140] $44.89432 + 0.15338544T/K$ [140] 212.007464 [140]

* Above the temperature of fusion, the heat capacity of $K_2CrO_{4(S2)}$ was assumed to be equal to that of $K_2CrO_{4(L)}$ to ensure a reasonable extrapolation of the Gibbs energy at high temperatures. In absence of this additional C_p range, the high-temperature allotrope would be calculated to be more stable than the pure liquid above 6814 K.

The temperature for the solid-solid transition reported by Żemczużny [132] was discarded since it is substantially higher than all other measurements from the literature.

The values of the enthalpy change for the solid-solid transition listed in Table 5.10 are somewhat different from each other [114, 134, 137, 140-142]. The measurements made by DSC were prioritized among all reported values since this technique is more accurate than DTA. The value of 6.908 kJ/mol obtained by Janz and Slowick [142] using DSC was discarded since it has large error bars according to these authors.

The standard enthalpy at 298.15 K of -1,403,700 J/mol for $\text{K}_2\text{CrO}_{4(\text{S}1)}$ was taken directly from the NBS Tables of chemical thermodynamic properties of Wagman et al. [149], since no experimental values were found in the literature. OQMD [128, 129] reported an enthalpy of formation at 0 K of -1,362,952 J/mol using DFT calculations. The corresponding value given in Materials Project [130] is -1,394,695 J/mol.

The standard entropy at 298.15 K ($S_{298.15\text{ K}}^\circ$) reported by Popov and Kolesov [150] (see Table 5.12) is in very good agreement with that in the book edited by Lax [137] (i.e. 200 J/mol.K), and also with that from Barin [127] (i.e. 199.995 J/mol.K). The value from Popov and Kolesov is the only experimental value found in the literature; it was obtained by integration of $\int_0^{298.15\text{ K}} \frac{C_P}{T} dT$, where the low-temperature heat capacity was measured by calorimetry.

To our knowledge, there are no other direct C_P measurements for K_2CrO_4 available in the literature. Heat content ($H_T - H_{298.15\text{ K}}$) measurements were conducted by Sirousse-Zia [140] using 99.5% certified material and enthalpimetric analysis in an ice calorimeter. This author obtained eleven experimental values for each phase ($\text{K}_2\text{CrO}_{4(\text{S}1)}$, $\text{K}_2\text{CrO}_{4(\text{S}2)}$, and $\text{K}_2\text{CrO}_{4(\text{L})}$), and derived a fit of $H_T - H_{298.15\text{ K}}$ as a function of temperature. For S_1 , between 517 and 888 K, $H_T - H_{298.15\text{ K}} = 0.8656 \times 10^{-5} T^3 - 0.5322 \times 10^{-2} T^2 + 39.044T - 10,967$ cal/mol (0.7%, empirical standard deviation of 15 calories). The corresponding value is 1.776 kJ/mol at 298.15K. The following new fit, which is null at 298.15K, was obtained by us: $0.030595227(T - 298.15)^2 + 162.5098706(T - 298.15)$ J/mol.

Sirousse-Zia [140] also derived the following fits : for S_2 , between 942 and 1202 K, $H_T - H_{298.15\text{ K}} = 0.1833 \times 10^{-1} T^2 + 10.730T + 4,290$ cal/mol (0.4%, empirical standard deviation of 11 calories); for the pure liquid, above 1261 K, $H_T - H_{298.15\text{ K}} = 50.671T - 9,122$ cal/mol (0.4%, empirical standard deviation of 11 calories). For each phase of K_2CrO_4 , the heat capacity expression (as a function of temperature) was derived (see Table 5.12) from the fits of $H_T - H_{298.15\text{ K}}$ given previously. Calculated values of $H_T - H_{298.15\text{ K}}$ are shown along with the available data in Figure 5.3. Our calculations somewhat underestimate the measurements of Sirousse-Zia [140] for the high-temperature allotrope and the pure liquid since the selected enthalpy changes for the solid-solid transition and the fusion are weighted averages of all available data from the literature and of our own DSC measurements.

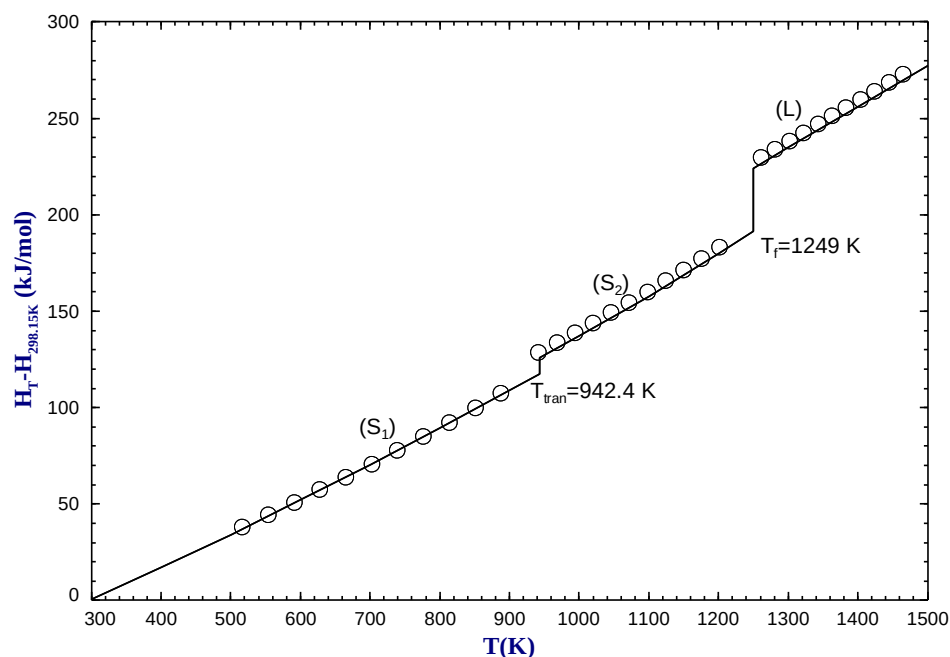


Figure 5.3 Calculated heat content $H_T - H_{298.15 \text{ K}}$ for K_2CrO_4 (enthalpies of transition are the weighted average of all available data presented in tables 5.10 and 5.11). Experimental data from [80] (○).

5.4.3 Sodium molybdate

5.4.3.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transitions for Na_2MoO_4

The temperatures and enthalpy changes for the various solid-solid transitions (S_1 - S_2 , S_2 - S_3 , and S_3 - S_4) of Na_2MoO_4 were measured by DSC in this work. These data along with all measurements available in the literature are shown in Tables 5.13, 5.14 and 5.15 respectively. Our experimental DSC thermogram is presented in the Supporting Information (Figure B2).

Table 5.13 Temperature and enthalpy change of transition S_1 - S_2 for Na_2MoO_4

$T_{\text{trans}} S_1 \rightarrow S_2$ (°C)	$\Delta H_{\text{trans}} S_1 \rightarrow S_2$ (kJ/mol)	Experimental Method	Reference
455.8	22.447	DSC (2 nd heating) 10°C/min	This work
456.7	22.097	DSC (3 rd heating) 10°C/min	This work
440	61.086	Heating or cooling curves	[134]
457.9 ± 2	26.65	DTA	[114]
454.9 ± 1	-	DTA 5°C/min	[151]
444.9 ± 2	21.76 ± 0.38	Drop calorimetry	[115]
460.9	-	DSC (cooling) 3°C/min	[97]
440.9 (run 1) 435.9 (run 2) 441.9 (run 3)	-	DTA (1.8°C/min and 10.2°C/min)	[152]
459.9	-	DTA (heating) 10°C/min	[93]
457.85	-	DSC 10°C/min	
509.9-529.9	-	Raman spectroscopy	[94]
456.9 ± 1	26.78 ± 0.38	DSC	[153]

		10, 5 and 2°C/min	
457.1	23.066	Weighted average of available data	This work

Table 5.14 Temperature and enthalpy change of transition S_2 - S_3 for Na_2MoO_4

$T_{\text{trans } S_2 \rightarrow S_3}$ (°C)	$\Delta H_{\text{trans } S_2 \rightarrow S_3}$ (kJ/mol)	Experimental Method	Reference
591.4	1.685	DSC (2 nd heating) 10°C/min	This work
591.4	1.700	DSC (3 rd heating) 10°C/min	This work
590.9 ± 2	1.88	DTA	[114]
579.9 ± 2	-	DTA 5°C/min	[151]
592.9 ± 3	2.09 ± 0.38	Drop calorimetry	[115]
591.9	-	DSC (cooling) 3°C/min	[97]
571.9 (run 1) 574.9 (run 2) 569.9 (run 3)	-	DTA 1.8 and 10.2°C/min	[152]
579.9	-	DTA (heating) 10°C/min	[93]
591.9	-	DSC	

		10°C/min	
549.9-639.9	-	Raman spectroscopy	[94]
592.9 ± 1	2.01 ± 0.33	DSC 10, 5 and 2°C/min	[153]
588.9	1.939	Weighted average of available data	This work

Table 5.15 Temperature and enthalpy change of transition S₃-S₄ for Na₂MoO₄

$T_{\text{trans S}_3 \rightarrow \text{S}_4}$ (°C)	$\Delta H_{\text{trans S}_3 \rightarrow \text{S}_4}$ (kJ/mol)	Experimental Method	Reference
642.4	8.316	DSC (2 nd heating) 10°C/min	This work
642.4	8.248	DSC (3 rd heating) 10°C/min	This work
641.9 ± 2	10.84	DTA	[114]
637.9 ± 2	-	DTA 5°C/min	[151]
641.9 ± 2	8.28 ± 0.46	Drop calorimetry	[115]
639.9	-	DSC (cooling) 3°C/min	[97]
641.9 ± 2	8.3 ± 0.4	Calorimetric (heat content) and spectroscopic measurements	[154]
622.9 (run 1)	-	DTA	[152]

625.9 (run 2) 618.9 (run 3)		1.8 and 10.2°C/min	
641.85	-	DTA (heating) 10°C/min	[93]
637.9	-	DSC 10°C/min	
669.9-676.9	-	Raman spectroscopy	[94]
639.9 ± 1	7.81 ± 1.25	DSC 10, 5 and 2°C/min	[153]
640.6	8.372	Weighted average of available data	This work

5.4.3.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for Na_2MoO_4

The properties of fusion (temperature and enthalpy change) were measured by [93, 97, 114, 115, 151-157]. The enthalpy of fusion was obtained using DTA [114], drop calorimetry [115], calorimetry [154], and DSC [153]. All data collected from the literature and our own DSC measurements are displayed in Table 5.16.

Table 5.16 Temperature and enthalpy of fusion for Na_2MoO_4

$T_f \text{ } S_4 \rightarrow L$ (°C)	$\Delta H_f \text{ } S_4 \rightarrow L$ (kJ/mol)	Experimental Method	Reference
688.2	18.637	DSC (2 nd heating) 10°C/min	This work
686.9	18.495	DSC (3 rd heating) 10°C/min	This work

688	-	Visual-polythermal method	[155]
690	-	DTA	[156]
692.9 ± 2	24.43	DTA	[114]
686.9 ± 1	-	DTA 5°C/min	[151]
688.9 ± 3	21.42 ± 0.5	Drop calorimetry	[115]
688.9	-	DSC (cooling) 3°C/min	[97]
685.9 ± 2	20.4 ± 0.4	Calorimetric (heat content) and spectroscopic measurements	[154]
687	-	Thermal analysis	[157]
671.9 (run 1) 674.9 (run 2) 667.9 (run 3)	-	DTA 1.8 and 10.2°C/min	[152]
679.9	-	DSC 10°C/min	[93]
684.9	-	DTA 10°C/min	
683.9 ± 1	20.73 ± 1.14	DSC 10, 5 and 2°C/min	[153]
686.9	20.582	Weighted average of available	This work

		data	

5.4.3.3 Recommended thermodynamic data for sodium molybdate Na_2MoO_4

Our selected thermodynamic data ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_P) for sodium molybdate (Na_2MoO_4) are shown in Table 5.17.

Table 5.17 Selected thermodynamic properties of Na_2MoO_4

Compound	<i>T</i> Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol)	$S_{298.15\text{ K}}^\circ$ (J/mol.K)	C_P (J/mol.K)
$\text{Na}_2\text{MoO}_{4(\text{S1})}$	298.15 to 730.2 (This work)	-1 465 870.0 [158]	159.4104 [159]	125.344272 + 0.07857552 <i>T</i> /K [115]
$\text{Na}_2\text{MoO}_{4(\text{S2})}$	298.15 to 730.2 730.2 to 862.1 (This work)	-1 442 803.9 (This work)	190.9990 (This work)	125.344272 + 0.07857552 <i>T</i> /K [115] -215.459264 + 0.50643136 <i>T</i> /K [115]
$\text{Na}_2\text{MoO}_{4(\text{S3})}$	298.15 to 730.2 730.2 to 862.1 862.1 to 913.7 (This work)	-1 440 864.7 (This work)	193.2486 (This work)	125.344272 + 0.07857552 <i>T</i> /K [115] -215.459264 + 0.50643136 <i>T</i> /K [115] 202.3 (This work)
$\text{Na}_2\text{MoO}_{4(\text{S4})}$	298.15 to 730.2 730.2 to 862.1 862.1 to 913.7 913.7 to 960.1 (This work)	-1 432 492.7 (This work)	202.4113 (This work)	125.344272 + 0.07857552 <i>T</i> /K [115] -215.459264 + 0.50643136 <i>T</i> /K [115] 202.3 (This work) 208.3 (This work)
$\text{Na}_2\text{MoO}_{4(\text{L})}$	298.15 to 730.2	-1 411 909.8 (This work)	223.8496 (This work)	125.344272 + 0.07857552 <i>T</i> /K [115]

	730.2 to 862.1			-215.459264 + 0.50643136T/K [115]
	862.1 to 913.7			202.3 (This work)
	913.7 to 960.1			208.3 (This work)
	960.1 to 2000 (This work)			213.0 [115]

For the temperature of the S_1 - S_2 transition, the values reported by Hare [134] and Iyer et al. [152] were not considered since they are lower by about 15°C than all other measurements, as seen in Table 5.13. The temperature from Lima et al. [94] was also discarded since it is much higher than all other data.

For the temperatures of the S_2 - S_3 and S_3 - S_4 transitions, the two values reported by Iyer et al. [152] were ignored since they are lower by about 19°C than all other measurements, as seen in Tables 5.14 and 5.15, respectively. The temperatures from Lima et al. [94] were also discarded since they differ significantly from the other data. Finally, the melting temperature of Iyer et al. (1990) [152], which is rather low, was excluded.

For each transition (S_1 - S_2 , S_2 - S_3 , S_3 - S_4 , and S_4 -L), the reported enthalpy changes are very similar (see Tables 5.13, 5.14, 5.15, and 5.16). Calorimetric measurements (such as heat content determinations) were favoured since the corresponding technique is static and, therefore, there should be no accumulation of errors. On the other hand, DSC and DTA are both dynamic techniques, and accumulation of errors may be quite high. It should be noted that the enthalpy change for the S_1 - S_2 transition measured by Hare [134] was discarded since it is substantially different from all other available measurements.

The molar enthalpy of dissolution of Na_2MoO_4 in a NaOH solution was measured at 298.15 K by Tangri et al. using an isoperibol calorimeter [158]. The molar enthalpy of solution at infinite dilution was measured as -11.79 ± 0.51 kJ/mol [158], and a standard enthalpy at 298.15 K of $-1,465.87$ kJ/mol was then derived for $\text{Na}_2\text{MoO}_{4(S1)}$. Using a cycle of calorimetric reactions, Koehler et al. [160] evaluated $\Delta H_{298.15\text{ K}}^\circ = -1,467.75$ kJ/mol. The value recommended in Barin's compilation tables [127] is $-1,469.00$ kJ/mol. The $\Delta H_{298.15\text{ K}}^\circ$ value reported by Tangri et al. [158] was selected in the present work. OQMD [128, 129] reported an enthalpy of formation at 0 K of -

1,560,168 J/mol using DFT. The corresponding value given in Materials Project [130] is -1,456,157 J/mol.

For the standard entropy at 298.15 K ($S_{298.15\text{ K}}^\circ$), Welle and King [159] reported a value of 159.4104 J/mol.K, estimated by integration of their low-temperature heat capacity measurements obtained by calorimetry. The Einstein and Debye functions were used over the extrapolated temperature range of 0K to 51K.

Using DSC, Gavrichev et al. [161] performed low-temperature C_P measurements from 14 to 297 K, and derived a $S_{298.15\text{ K}}^\circ$ value of 149.9 ± 0.2 J/mol.K.

Finally, the $S_{298.15\text{ K}}^\circ$ value obtained by Weller and King [159], which is close to the value of 159.410 J/mol.K recommended in Barin's compilation tables [127], was selected in this work.

Using drop calorimetry in an ice calorimeter, Denielou et al. [115] performed heat content measurements ($H_T - H_{273.15\text{ K}}$) for Na_2MoO_4 , and derived fits of their data along with C_P expressions (as a function of temperature). The stability of the salts was verified by XRD analyses.

For $\text{Na}_2\text{MoO}_{4(\text{S}_1)}$, based on eleven measurements between 427 and 709K, $H_T - H_{273.15\text{ K}} = 9.391 \times 10^{-3}T^2 + 29.958T - 8,987$ cal/mol (0.3%, empirical standard deviation of 5 calories). This fit was assumed to be valid from 298.15 K to our selected temperature of 730.2 K for the S_1 - S_2 transition.

Extrapolation to 296.5 K of the heat capacity expression $C_{P(\text{S}_1)} = 0.07857552 T + 125.344272$ (valid from 427 K to 709 K) given by Denielou et al. [115] gives a value of 148.642 J/mol.K, which agrees well with the heat capacity measurement of Weller and King [159]. Gavrichev et al. [161] measured at 298.15 K a value of 131.813 J/mol.K, which is about 17 J/mol.K lower.

For $\text{Na}_2\text{MoO}_{4(\text{S}_2)}$, based on twelve measurements between 734 and 857 K, $H_T - H_{273.15\text{ K}} = 6.052 \times 10^{-2}T^2 - 51.496T + 28,343$ cal/mol (0.13%, empirical standard deviation of 11 calories). This fit was assumed to be valid from 730.2 K to our selected temperature of 862.1 K for the S_2 - S_3 transition.

For $\text{Na}_2\text{MoO}_{4(\text{S}_3)}$, based on ten measurements between 870 and 907 K, $H_T - H_{273.15\text{ K}} = 1.065 \times 10^{-1}T^2 - 1.409 \times 10^2T + 71,830$ cal/mol (0.14%, empirical standard deviation of 9 calories). This fit was assumed to be valid from 862.1 K to our selected temperature of 913.7 K for the S_3 - S_4 transition.

A typo was detected in the article of Denielou et al. [115]. The original constant of 7,183 cal/mol in the fit provided for $\text{Na}_2\text{MoO}_{4(\text{S}_3)}$ corresponded to negative values of $(H_T - H_{273.15\text{K}})$. Adjusting this constant to 71,830 cal/mol permitted us to reproduce (within the reported error bars) the experimental enthalpy changes of Denielou et al. [115] for the $\text{S}_2\text{-S}_3$ and $\text{S}_3\text{-S}_4$ transitions (The two temperatures used for these calculations were those reported by the authors.)

For $\text{Na}_2\text{MoO}_{4(\text{S}_4)}$, based on nine measurements between 920 and 960 K, $H_T - H_{273.15\text{K}} = -1.141 \times 10^{-1}T^2 + 2.643 \times 10^2T + 1.123 \times 10^5$ cal/mol (0.16%, empirical standard deviation of 18 calories). This fit was assumed to be valid from 913.7 K to our selected temperature of fusion of 960.1 K.

A marked decrease of C_P as a function of temperature was observed between the allotropes (S_3) and (S_4), owing to the mathematical expressions of $(H_T - H_{273.15\text{K}})$ proposed by Denielou et al. [115]. Since the temperature ranges of validity were very limited (from 870 to 907 K for S_3 , and from 920 to 960 K for S_4), the corresponding values of $(H_T - H_{273.15\text{K}})$ were refitted by us using a linear expression ($a + bT$), thus leading to constant heat capacity values. Our new fits of $(H_T - H_{273.15\text{K}})$ are $202.3T - 51,169$ (J/mol) for S_3 , and $208.3T - 48,117$ (J/mol) for S_4 . The corresponding C_P values are 202.3 J/mol.K and 208.3 J/mol.K, respectively (see Table 5.17).

For $\text{Na}_2\text{MoO}_{4(\text{L})}$, based on fourteen measurements above 1091 K, $H_T - H_{273.15\text{K}} = 48.943T - 9,737$ cal/mol (0.1%, empirical standard deviation of 29 calories).

Calculated values of $H_T - H_{298.15\text{K}}$ are shown along with the available measurements in Figure 5.4. This figure includes the heat contents $H_T - H_{298.15\text{K}}$ measured by Iyer et al. [152] as well as the $H_T - H_{298.15\text{K}}$ values obtained by conversion of the $H_T - H_{273.15\text{K}}$ data of Denielou et al. [115] [$H_T - H_{298.15\text{K}} = (H_T - H_{273.15\text{K}}) - (H_{298.15\text{K}} - H_{273.15\text{K}})$]. These two series of data are in good agreement.

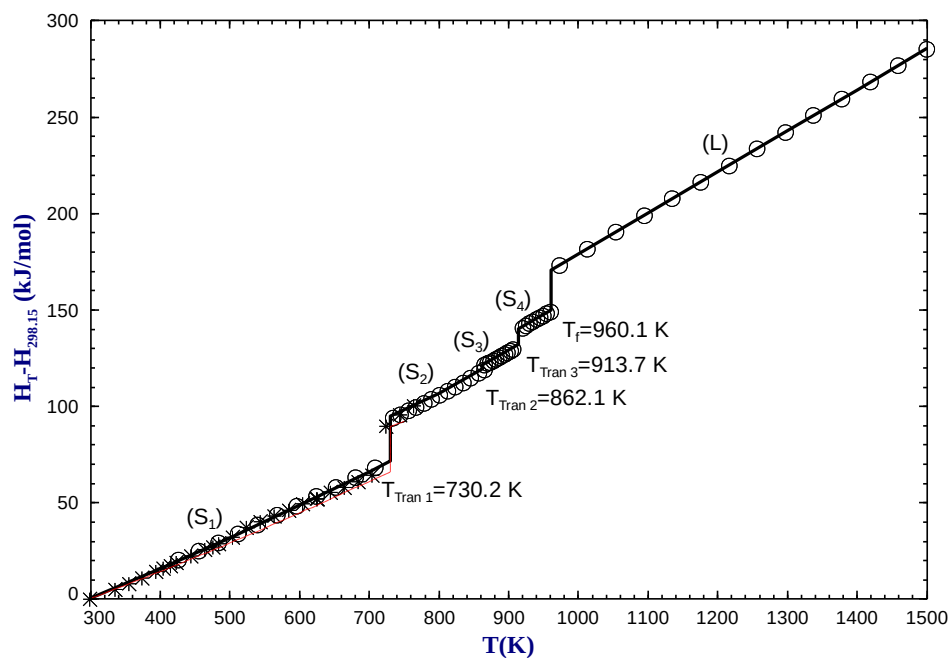


Figure 5.4 Calculated heat content $H_T - H_{298.15K}$ for Na_2MoO_4 (enthalpies of transition are the weighted average of all available data presented in tables 5.13 to 5.16). Experimental data from [115] ($\circ$) and [152] ($\ast$). Red dashed line: $H_T - H_{298.15K}$ fit of low-temperature heat capacity data shown in Figure 5.5.

The calculated heat capacity at low temperatures for $\text{Na}_2\text{MoO}_{4(S1)}$ is shown in Figure 5.5 along with the measurements of Weller and King [159], Gavrichev et al. [161], and Zhidikova and Kuskov [162].

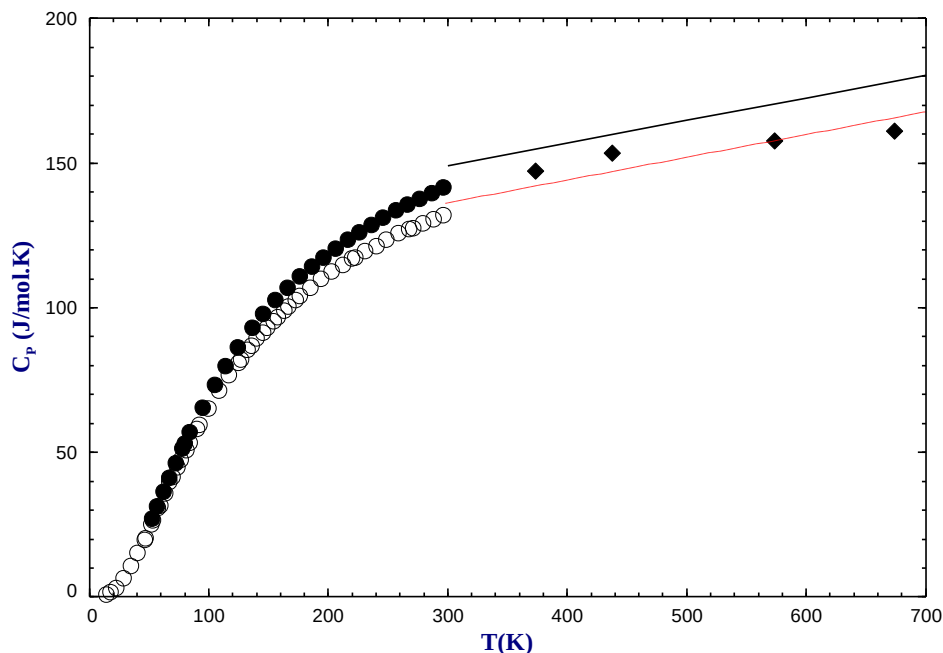


Figure 5.5 Calculated heat capacity at low temperatures for $\text{Na}_2\text{MoO}_4(\text{s1})$. Experimental data from [159] (●), [161] (○), and [162] (◆). Red dashed line: best linear fit of CP data above room temperature.

In Figure 5.4, the black full lines correspond to our final calculations while the red dashed line corresponds to heat contents $H_T - H_{298.15\text{K}}$ obtained from the fit of the low-temperature C_P data measured by [159], [161], and [162], and shown in Figure 5.5. An average deviation of about 3.7 kJ/mol is observed for the red dashed line, which is substantially higher than the error of about 20 J/mol reported by [115]. This lends support to our final calculations displayed in Figure 5.4 and

Figure 5.5.

The heat content measurements of Iyer et al. [152] were carried out over the temperature range 335 K to 760 K using drop calorimetry in a high-temperature Calvet calorimeter. These authors observed transitions at 520 ± 5 K and 720 ± 5 K. The first transition (at about 520 K) has not been reported previously while the DTA study of the same authors from 300 K to 973 K revealed the presence of three solid-solid transitions (at about 713, 845 and 896 K). According to Iyer et al. [152], the first transition (at about 520 K) was not observed in their calorimetric study owing to the sensitivity being insufficient to detect a small enthalpy change for a small sample size. For the second transition (at about 720 K), there is good agreement between the calorimetric and DTA

studies of Iyer et al. [152], and also with the calorimetric measurements of Denielou et al. [115] using drop calorimetry in an ice calorimeter. Finally, the transition at about 520 K reported by Iyer et al. [152] was ignored in the present work, and only three solid-solid transitions (corresponding to the four allotropes S_1 , S_2 , S_3 , and S_4) were considered.

5.4.4 Potassium molybdate

5.4.4.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transitions for K_2MoO_4

The temperatures and enthalpy changes for the various solid-solid transitions (S_1 - S_2 , S_2 - S_3 , and S_3 - S_4) of K_2MoO_4 were measured by DSC in the present work. These measurements along with all data collected from the literature are displayed in Tables 5.18, 5.19 and 5.20, respectively. Our experimental DSC thermogram is provided in the Supporting Information (Figure B3).

Table 5.18 Temperature and enthalpy change of transition S_1 - S_2 for K_2MoO_4

$T_{\text{trans}} S_1 \rightarrow S_2$ (°C)	$\Delta H_{\text{trans}} S_1 \rightarrow S_2$ (kJ/mol)	Experimental Method	Reference
325.4	2.338	DSC (2 nd heating) 10°C/min	This work
322.2	2.236	DSC (3 rd heating) 10°C/min	This work
327 ± 1.5	-	Thermal study	[163]
323	-	Thermal analysis (cooling)	[164]
321	-	Thermal analysis	[120]
323	-	DTA	[151]
295.9 ± 2	11.34	DTA	[114]

282.9	8.27 ± 0.10	DTA Heating $0.5^{\circ}\text{C}/\text{min}$ Cooling $0.42^{\circ}\text{C}/\text{min}$	[165]
322.9 ± 1	11.34 ± 1.62	DSC 10 and $5^{\circ}\text{C}/\text{min}$	[101]
323.5	11.340	Weighted average of available data	This work

Table 5.19 Temperature and enthalpy change of transition S_2 - S_3 for K_2MoO_4

$T_{\text{trans}} S_2 \rightarrow S_3$ ($^{\circ}\text{C}$)	$\Delta H_{\text{trans}} S_2 \rightarrow S_3$ (kJ/mol)	Experimental Method	Reference
454.8	0.980	DSC (2 nd heating) $10^{\circ}\text{C}/\text{min}$	This work
455.1	0.978	DSC (3 rd heating) $10^{\circ}\text{C}/\text{min}$	This work
454 ± 1.5	-	Thermal study	[163]
458	-	Thermal analysis (cooling)	[164]
439	-	Thermal analysis	[120]
438	-	DTA	[151]
451.9 ± 2	1.13	DTA	[114]
456.9	0.64 ± 0.03	DTA Heating $0.5^{\circ}\text{C}/\text{min}$ Cooling $0.42^{\circ}\text{C}/\text{min}$	[165]

452.9 ± 2	1.04 ± 0.06	DSC 10 and 5°C/min	[101]
454.7	1.018	Weighted average of available data	This work

Table 5.20 Temperature and enthalpy change of transition S_3 - S_4 for K_2MoO_4

$T_{\text{trans } S_3 \rightarrow S_4}$ (°C)	$\Delta H_{\text{trans } S_3 \rightarrow S_4}$ (kJ/mol)	Experimental Method	Reference
-	-	DSC (2 nd heating) 10°C/min	This work
-	-	DSC (3 rd heating) 10°C/min	This work
479.0 ± 1.5	-	Thermal study	[163]
480	-	Thermal analysis (cooling)	[164]
475	-	Thermal analysis	[120]
462	-	DTA	[151]*
475.9 ± 10	-	-	Reported from “V. P. Glushko (VINITI, Moscow, 1981–1982) volume 10” in [101]
479.9	0.024	DSC 5°C/min	[101]

* Another solid-solid transition at 480°C, which was not considered in this work, has been reported [151].

The experimental data in Tables 5.18, 5.19, and 5.20 suggest that there are three different solid-solid transitions for K_2MoO_4 . According to our high-temperature XRD measurements (at 465 and 500°C), there are only two solid-solid transitions. Furthermore, in the second and third heating/cooling runs of our two DSC experiments, the S_3 - S_4 transition was never observed. While performing DSC measurements with a heating/cooling rate of 5 K/min, Gavrichev et al. [101] did observe the S_3 - S_4 transition and reported an extremely low enthalpy change of 0.024 kJ/mol [101]. Other studies reported a similar transition temperature [120, 151, 163, 164] but did not measure the corresponding enthalpy change.

In most studies reporting the S_3 - S_4 transition, the purity of the reagents was not indicated, and thus this transition may be due to the presence of impurities. Finally, based on our XRD and DSC measurements, only two solid-solid transitions were considered for K_2MoO_4 in the present work. Note that, if a S_3 - S_4 transition were taken into account, it would have very little impact on our future calculations related to high temperature corrosion, since the corresponding enthalpy change would be very small (0.024 kJ/mol) and the S_3 allotrope would be stable over a limited temperature range of less than 25°C (i.e. between about 455 and 478°C).

5.4.4.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for K_2MoO_4

The properties of fusion (temperature and enthalpy change) were measured by [101, 114, 120, 154-157, 163-165]

The heat of fusion was measured by DTA [114, 165], calorimetry [154], and DSC [101]. All experimental data from the literature and our own DSC measurements are gathered in Table 5.21.

Table 5.21 Temperature and enthalpy of fusion for K_2MoO_4

$T_f \ S_3 \rightarrow L$ (°C)	$\Delta H_f \ S_3 \rightarrow L$ (kJ/mol)	Experimental Method	Reference
927.1	30.460	DSC (2 nd heating) 10°C/min	This work
927.8	28.983	DSC (3 rd heating)	This work

		10°C/min	
819 ± 1.5	-	Thermal study	[163]
926	-	Thermal analysis (cooling)	[164]
936	-	Thermal analysis	[120]
926	-	Visual-polythermal method	[155]
926	-	Heating curves	[156]
926	38.702	DTA	[114]
925.9 ± 1	38.70	(DTA) Heating 0.5°C/min Cooling 0.42°C/min	[165]
927.9 ± 2	34.70 ± 0.7	Calorimetric (heat content) and spectroscopic measurements	[154]
926	-	Thermal analysis	[157]
930.9 ± 1	40.14 ± 1.25	DSC 10 and 5°C/min	[101]
927.8	34.626	Weighted average of available data	This work

5.4.4.3 Recommended thermodynamic data for potassium molybdate K_2MoO_4

Our selected thermodynamic data ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$ and C_P) for potassium molybdate (K_2MoO_4) are shown in Table 5.22.

Table 5.22 Selected thermodynamic properties of K_2MoO_4

Compound	<i>T</i> Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol)	$S_{298.15\text{ K}}^\circ$ (J/mol.K)	C_p (J/mol.K)
$K_2MoO_4(S_1)$	298.15 to 596.6 (This work)	-1 497 846.1 (This work)	199.3000 [101]	$113.495184 + 0.096876336T/K$ $+ 729689.6 (T/K)^{-2}$ (This work)
$K_2MoO_4(S_2)$	298.15 to 727.9 (This work)	-1 486 506.1 (This work)	218.3077 (This work)	$113.495184 + 0.096876336T/K$ $+ 729689.6 (T/K)^{-2}$ (This work)
$K_2MoO_4(S_3)$	298.15 to 730.2 (This work) 730.2 to 836.8 (This work) 836.8 to 1201 (This work)	-1 485 488.0 (This work)	219.7063 (This work)	$113.495184 + 0.096876336T/K$ $+ 729689.6 (T/K)^{-2}$ (This work) $-227.308352 + 0.524732176T/K$ $+ 729689.6 (T/K)^{-2}$ (This work) $196.450912 + 0.018300816T/K$ $+ 729689.6(T/K)^{-2}$ (This work)
$K_2MoO_4(L)$	298.15 to 730.2 (This work) 730.2 to 836.8 (This work) 836.8 to 1201 (This work) 1201 to 1500 (This work)	-1 450 837.7 (This work)	248.5872 (This work)	$113.495184 + 0.096876336T/K$ $+ 729689.6 (T/K)^{-2}$ (This work) $-227.308352 + 0.524732176T/K$ $+ 729689.6 (T/K)^{-2}$ (This work) $196.450912 + 0.018300816T/K$ $+ 729689.6(T/K)^{-2}$ (This work) $204.672872 + 0.0150624T/K$ (This work)

For the temperature of the S_1 - S_2 transition, the values of Riccardi and Sinistri [114] and Isozaki and Ozawa [165], which are lower by about 30°C than all other measurements in Table 5.18, were not

considered. For the temperature of the S₂-S₃ transition, the values of Schmitz-Dumont and Weeg [120], and of Caillet [151] were not considered (see Table 5.19). Finally, the temperature of fusion measured by Klooster [163] was excluded since it is lower by about 107°C than all other data shown in Table 5.21.

The enthalpy changes for the S₁-S₂, S₂-S₃, and S₃-L transitions reported in Tables 5.18, 5.19, and 5.21 are very similar. Again, measurements carried out by calorimetry [154] (such as heat content determinations) were favoured since this technique is static and thus more accurate than DSC or DTA, which are both dynamic techniques.

For the enthalpy change of the S₁-S₂ transition, our two DSC measurements were discarded since they are five times lower than the values of Riccardi and Sinistri [114] and Gavrichev et al. [101]. In particular, the two measurements of Gavrichev et al. [101] were obtained using two different heating/cooling rates (5 and 10°C/min), and corresponded to two very similar enthalpy changes : 12.53 ± 0.17 kJ/mol and 12.57 ± 0.15 kJ/mol respectively. For the enthalpy change of the S₂-S₃ transition, the value reported by Isozaki and Ozawa [165] was ignored (see Table 5.19).

The standard enthalpy at 298.15 K ($\Delta H_{298.15K}^\circ$) of K₂MoO_{4(S1)} was estimated as -1,497,846 J/mol as follows. Nelson et al. [126] measured by calorimetry the enthalpy of dissolution of K₂MoO_{4(S1)} in a 10⁻³ M OH_(aq)⁻ solution. These authors reported an enthalpy change of -3,974.8 J/mol for the reaction $K_2MoO_{4(S1)} \rightarrow 2K_{(aq)}^+ + MoO_{4(aq)}^{2-}$. According to the FactSage databases [42], $\Delta H_{298.15K}^\circ(K_{(aq)}^+) = -251,968.4$ J/mol and $\Delta H_{298.15K}^\circ(MoO_{4(aq)}^{2-}) = -997,884.0$ J/mol. There is no recommended value of $\Delta H_{298.15K}^\circ$ for K₂MoO_{4(S1)} in Barin's compilation tables [127]. OQMD [128, 129] reported an enthalpy of formation at 0 K of -1,575,702 J/mol using DFT. The corresponding value given in Materials Project [130] is -1,493,303 J/mol.

The standard entropy at 298.15 K ($S_{298.15K}^\circ$) of K₂MoO_{4(S1)} was set to the value of 199.3 J/mol.K reported by Gavrichev et al. [101]. These authors derived this value by integration of $\int_{0K}^{298.15K} \frac{C_p}{T} dT$ using their low-temperature heat capacity data obtained by DSC. To our knowledge, this is the only experimental value available in the literature. $S_{298.15K}^\circ$ was estimated by us using two different exchange reactions, for which $\Delta S = 0$ was assumed at 298.15 K. We derived a value of 182.790 J/mol.K from the exchange reaction $Na_2MoO_{4(S1)} + K_2CrO_{4(S1)} \rightarrow K_2MoO_{4(S1)} + Na_2CrO_{4(S1)}$, and a value of 180.247 J/mol.K from the exchange reaction

$\text{Na}_2\text{MoO}_4(\text{S}_1) + 2\text{KCl}(\text{S}) \rightarrow \text{K}_2\text{MoO}_4(\text{S}_1) + 2\text{NaCl}(\text{S})$. The standard entropies at 298.15K of $\text{Na}_2\text{MoO}_4(\text{S}_1)$, $\text{K}_2\text{CrO}_4(\text{S}_1)$ and $\text{Na}_2\text{CrO}_4(\text{S}_1)$ were assessed by us in this work, and those of $\text{KCl}(\text{S})$ and $\text{NaCl}(\text{S})$ were taken from the FTsalt thermodynamic database [42]. Our two derived $S_{298.15\text{ K}}^\circ$ values are very rough estimates. These are lower than the value reported by Gavrichev et al [101].

The latter value, which was selected in this work, is probably somewhat too low since the experimental $S_{298.15\text{ K}}^\circ$ value of Gavrichev et al [161] for Na_2MoO_4 was lower by about 10 J/mol.K than the values of [127] and [159] favored in this work.

To our knowledge, the low-temperature data of Gavrichev et al [101] are the only direct heat capacity measurements available for K_2MoO_4 . In the present work, the heat capacity (as a function of temperature) of K_2MoO_4 was assessed from the following exchange reactions, assuming that $\Delta C_p = 0$ at all temperatures : $\text{Na}_2\text{MoO}_4(\text{S}) + 2\text{KCl}(\text{S}) \rightarrow \text{K}_2\text{MoO}_4(\text{S}) + 2\text{NaCl}(\text{S})$ for the solid phases (S_1 , S_2 , and S_3), and $\text{Na}_2\text{MoO}_4(\text{L}) + 2\text{KCl}(\text{L}) \rightarrow \text{K}_2\text{MoO}_4(\text{L}) + 2\text{NaCl}(\text{L})$ for the pure liquid. The heat capacity of Na_2MoO_4 was evaluated in the present work, and those of KCl and NaCl were taken from the FTsalt database [42].

In Figure 5.6, the calculated heat capacity of solid K_2MoO_4 at low temperatures is compared to three series of measurements (3, 4 and 6) conducted by Gavrichev et al. [101] using DSC. These authors performed six different series of measurements at low temperatures: series 1 between 78.83 and 215.59 K, series 2 between 132.27 and 215.40 K, series 3 between 8.97 and 75.08 K, series 4 between 174.38 and 342.90 K, series 5 between 245 and 257.31 K, and series 6 between 99.83 and 116.16 K. Agreement from room temperature to 342.90 K (maximum temperature investigated by Gavrichev et al) is satisfactory.

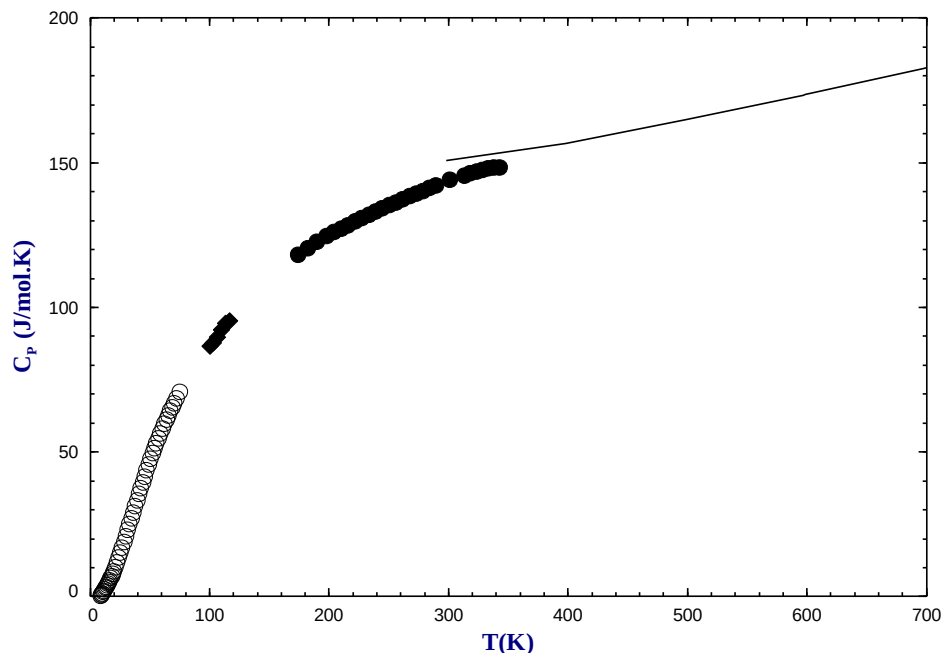


Figure 5.6 Calculated heat capacity at low temperatures for $\text{K}_2\text{MoO}_4(\text{S}_1)$. Experimental data from [101] (series 3 : $\circ$, series 4 : $\bullet$, and series 6 : $\blacklozenge$).

5.4.5 Sodium tungstate

5.4.5.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transitions for Na_2WO_4

The temperatures and enthalpy changes for the solid-solid transitions ($\text{S}_1\text{-S}_2$ and $\text{S}_2\text{-S}_3$) of Na_2WO_4 were measured by DSC in the present work. These measurements along with all data collected from the literature are displayed in Tables 5.23 and 5.24, respectively. Our experimental DSC thermogram is displayed in the Supporting Information (Figure B4).

Table 5.23 Temperature and enthalpy change of transition $\text{S}_1\text{-S}_2$ for Na_2WO_4

$T_{\text{trans}} \text{ S}_1 \rightarrow \text{S}_2$ ($^{\circ}\text{C}$)	$\Delta H_{\text{trans}} \text{ S}_1 \rightarrow \text{S}_2$ (kJ/mol)	Experimental Method	Reference
-	28.93	DSC (2 nd heating) 10 $^{\circ}\text{C}/\text{min}$	This work

-	28.66	DSC (3 rd heating) 10°C/min	This work
564	-	Cooling curves	[107]
587	-	Cooling curves*	[166]
587.6	30.851	DTA	[167]
579	39.790	Heating or cooling curves	[134]
588	31.380 ± 0.146	DTA** 1°C/min	[146]
591	34.434	DTA	[114]
585.9 ± 3	31.506 ± 0.502	Drop calorimetry	[115]
587.9	-	DSC (cooling) 0.3°C/min	[97]
559.9	-	Raman spectroscopy	[94]
-	3.3	Thermal analysis (DSC) 8-10°C/min	[168]
589	-	DSC (heating) 0.1°C/min	[106]
588.3	31.471^{***}	Weighted average of available data	This work

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

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

*** See explanation in text

Table 5.24 Temperature and enthalpy change of transition S₂-S₃ for Na₂WO₄

$T_{\text{trans}} \text{ S}_2 \rightarrow \text{S}_3$ (°C)	$\Delta H_{\text{trans}} \text{ S}_2 \rightarrow \text{S}_3$ (kJ/mol)	Experimental Method	Reference
-	-	DSC (2 nd heating) 10°C/min	This work
-	-	DSC (3 rd heating) 10°C/min	This work
564-588	-	Cooling curves	[107]
591	-	Cooling curves*	[166]
588.8	4.113 ± 0.015	DTA	[167]
589	4.142 ± 0.146	DTA 1°C/min	[146]
589.9	-	DSC (cooling) 0.3°C/min	[97]
591	-	DSC (heating) 0.1°C/min	[106]

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

5.4.5.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for Na₂WO₄

The properties of fusion (temperature and enthalpy change) were measured by [97, 107, 114, 115, 123, 146, 157, 166-169]. The heat of fusion was obtained by DTA [114, 146, 167, 168] and drop calorimetry [115]. All experimental data collected from the literature and our own DSC measurements are compiled in Table 5.25.

Table 5.25 Temperature and enthalpy of fusion for Na₂WO₄

T_f S ₃ → L (°C)	ΔH_f S ₃ → L (kJ/mol)	Experimental Method	Reference
690.8	24.47	DSC (2 nd heating) 10°C/min	This work
690.9	23.85	DSC (3 rd heating) 10°C/min	This work
698	-	Cooling curves	[107]
694	-	Cooling curves	[166]
695.5	23.799 ± 0.015	DTA	[167]
698	-	Visual-polythermal analysis	[169]
696	31.254 ± 0.146	DTA 1°C/min	[146]
698	31.464	DTA	[114]
693	-	Visual-polythermal analysis	[123]
689	-	Thermal analysis	[157]
693.9 ± 2	27.865 ± 0.586	Drop calorimetry	[115]
693.9	-	DSC (cooling) 0.3°C/min	[97]
695.9 ± 2	34 ± 3.5	Thermal analysis (DTA) 8-10°C/min	[168]
694.2	27.454	Weighted average of available data	This work

5.4.5.3 Recommended thermodynamic data for sodium tungstate Na_2WO_4

Our selected thermodynamic data ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_P) for sodium tungstate (Na_2WO_4) are given in Table 5.26.

Table 5.26 Selected thermodynamic properties of Na_2WO_4

Compound	<i>T</i> Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol)	$S_{298.15\text{ K}}^\circ$ (J/mol.K)	C_P (J/mol.K)
$\text{Na}_2\text{WO}_4(\text{S}_1)$	298.15 to 861.5 (This work)	-1 544 732.8 [170]	161.0840 [171]	$130.180976 + 0.0673373T/\text{K}$ (This work)
$\text{Na}_2\text{WO}_4(\text{S}_2)$	298.15 to 861.5 861.5 to 967.4 (This work)	-1 513 262.2 (This work)	197.6140 (This work)	$130.180976 + 0.0673373T/\text{K}$ (This work) $-29.723136 + 0.25580976T/\text{K}$ (This work)
$\text{Na}_2\text{WO}_4(\text{L})$	298.15 to 861.5 861.5 to 967.4 967.4 to 2000 (This work)	-1 485 808.5 (This work)	225.9929 (This work)	$130.180976 + 0.0673373T/\text{K}$ (This work) $-29.723136 + 0.25580976T/\text{K}$ (This work) 216.18728 (This work)

Various studies were conducted to identify the number of solid-solid transitions. Some authors reported a single solid-solid transition [94, 114, 115, 134, 168] while others reported two such transitions [97, 106, 146, 166, 167].

Denielou et al. [115] used drop calorimetry to measure heat contents ($H_T - H_{273.15\text{ K}}$) whereas Riccardi and Sinistri [114] performed DTA measurements; both studies reported a single solid-solid transition (see Table 5.23). The DSC analyses of Bottelberghs and van Buren [97] were able to separate the peaks corresponding to the S_1 - S_2 and S_2 - S_3 transitions using a very low heating rate of $0.3^\circ\text{C}/\text{min}$. They estimated the temperature range of stability of the S_2 allotrope to be only about 2°C . According to Bottelberghs and van Buren [97], the previous studies did not observe the S_2 - S_3 transition because their calorimetric apparatuses were not calibrated with Zn, thus preventing them from measuring quantitatively and separately all solid-solid transitions.

Goranson and Kracek [167] observed large overheating and undercooling effects for the S_2 - S_3 transition on their differential heating and cooling curves; they reported a difference of only 1.2°C

between their temperatures for the S_1 - S_2 and S_2 - S_3 transitions. Similarly, the DSC measurements of Hämmer and Höppe [106] at a heating rate of $0.1^\circ\text{C}/\text{min}$ showed these two solid-solid transitions, with a temperature difference of only 2°C .

Our DSC measurements for Na_2WO_4 were performed at a heating/cooling rate of $10^\circ\text{C}/\text{min}$. One solid-solid transition was observed upon heating whereas two different solid-solid transitions were observed upon cooling. The presence of two exothermic events in our DSC cooling curves indicates that both phase transitions were reversible [106].

For the temperature of the S_1 - S_2 transition, the value of Hare [134], which is relatively low compared to all other available data, was discarded. Also, the value of Suponitskiy et al. [168] for the enthalpy change of the S_1 - S_2 transition was not considered since it is substantially different from all other measurements (see Table 5.23).

Our weighted averages of the temperatures for the S_1 - S_2 and S_2 - S_3 transitions are 588.4°C and 588.7°C (see Tables 5.23 and 5.24), respectively, with a temperature difference of only 0.3°C . Hence, only two allotropes for Na_2WO_4 were considered in the present work: the low-temperature allotrope S_1 and the high-temperature allotrope S_3 (which was renamed S_2 for the sake of clarity, as seen in Table 5.26). Nolte and Kordes [146], and Goranson and Kracek [167] are the only authors who were able to measure the enthalpy changes of the S_1 - S_2 and S_2 - S_3 transitions. Our selected enthalpy change for the S_1 - S_2 transition (where the notation “ S_2 ” now refers to the high-temperature allotrope S_3) is the sum of the two enthalpy changes for the S_1 - S_2 and S_2 - S_3 transitions reported in [146] and [167]. (A weighted average of these two series of data was used).

For both Na_2WO_4 and Na_2MoO_4 , the enthalpy change of the S_1 - S_2 transition is higher than the enthalpy of fusion. Therefore, for both compounds, the entropy change of the S_1 - S_2 transition exceeds the entropy of fusion. For Na_2WO_4 , Goranson and Kracek [167] estimated the volume changes related to the S_1 - S_2 transition and to the fusion using their calorimetric data and the Clausius-Clapeyron relation. Based on these values (see Table 5.27), the molar volume change

associated with the S_1 - S_2 transition is larger than the molar volume change upon melting. This explains the ranking of the corresponding entropy changes. It is very likely that the same phenomenon occurs for Na_2MoO_4 .

Table 5.27 Volume change of Na_2WO_4

Transition	Volume change (cm^3/g)	Volume change (cm^3/mol)
$\text{Na}_2\text{WO}_4(\text{S}_1 \rightarrow \text{S}_2)$	0.035 [167]	10.284
$\text{Na}_2\text{WO}_4(\text{S}_3 \rightarrow \text{L})$	0.018 [167]	5.289

The standard enthalpy at 298.15 K ($\Delta H_{298.15\text{ K}}^\circ$) of $\text{Na}_2\text{WO}_{4(\text{S}1)}$ was estimated by JANAF [170] from the reaction $\text{H}_2\text{WO}_{4(\text{S})} + 2 \text{NaCl}_{(\text{S})} = \text{Na}_2\text{WO}_{4(\text{S}1)} + 2 \text{HCl}_{(\text{aq.}, 12.731 \text{ H}_2\text{O})}$, using $\Delta H_{298.15}^\circ(\text{H}_2\text{WO}_{4(\text{S})}) = -1131.77 \text{ kJ/mol}$ and $\Delta H_{298.15}^\circ(\text{NaCl}_{(\text{S})}) = -411.12 \text{ kJ/mol}$ both taken from [170], the heat of reaction $\Delta_r H_{303.15\text{ K}}^\circ = 81.34 \pm 0.33 \text{ kJ/mol}$ measured by Koehler et al. [160], and $\Delta H_{298.15}^\circ(\text{HCl}_{(\text{aq.})}) = -74.843 \pm 62.76 \text{ kJ/mol}$ provided in [172].

The enthalpy change at 298.15 K of the reaction $\text{W}_{(\text{S})} + 2 \text{NaOH}_{(\text{aq})} + 2 \text{H}_2\text{O}_{(\text{l})} = \text{Na}_2\text{WO}_{4(\text{aq})} + 3 \text{H}_{2(\text{g})}$ was measured by calorimetry as $-29.288 \pm 6.276 \text{ kJ/mol}$ [173]. The heat of solution for the reaction $\text{Na}_2\text{WO}_{4(\text{S}1)} = \text{Na}_2\text{WO}_{4(\text{aq})}$ was then measured as $-7.113 \pm 0.418 \text{ kJ/mol}$, which finally permitted to derive a value of $-1,541,386 \text{ J/mol}$ for $\Delta H_{298.15}^\circ(\text{Na}_2\text{WO}_{4(\text{S}1)})$. This latter value is close to the value of $-1,544,732 \text{ J/mol}$ recommended by JANAF [170].

Using a cycle of calorimetric reactions, Koehler et al. [160] estimated $\Delta H_{298.15\text{ K}}^\circ(\text{Na}_2\text{WO}_{4(\text{S}1)})$ as $-1,586,573 \text{ J/mol}$.

Graham and Hepler [174] measured by calorimetry at 298.15 K the enthalpy of dissolution of $\text{Na}_2\text{WO}_{4(\text{S}1)}$ in small concentrations of NaOH or in 0.005-0.01 M NH_4OH , according to the reaction $\text{Na}_2\text{WO}_{4(\text{S}1)} \rightarrow 2\text{Na}_{(\text{aq})}^+ + \text{WO}_{4(\text{aq})}^{2-}$. From their experimental enthalpy change for the reaction

$\text{H}_2\text{WO}_{4(\text{S})} + 2 \text{OH}^-_{(\text{aq})} = \text{WO}_4^{2-}_{(\text{aq})} + 2 \text{H}_2\text{O}(\text{l})$ and the standard enthalpies at 298.15 K of $\text{H}_2\text{WO}_{4(\text{S})}$, OH^- and H_2O taken from [175], they first estimated $\Delta H^\circ_{298.15\text{K}}(\text{WO}_4^{2-}_{(\text{aq})})$. The obtained value was consistent with that of the Bureau of Standards [175]. Then, from the latter value, the standard enthalpy at 298.15 K of $\text{Na}^+_{(\text{aq})}$ provided by [175] and their measured enthalpy of dissolution of $\text{Na}_2\text{WO}_{4(\text{S1})}$ (-6.694 ± 0.418 kJ/mol), they assessed $\Delta H^\circ_{298.15\text{K}}(\text{Na}_2\text{WO}_{4(\text{S1})})$ as -1,588,246 J/mol.

Finally, the $\Delta H^\circ_{298.15\text{K}}$ value recommended by JANAF [170] was selected in this work. Indeed, according to JANAF [170], Koehler et al. [160] and Graham and Hepler [174] used an erroneous value of -1172.357 kJ/mol for $\Delta H^\circ_{298.15\text{K}}(\text{H}_2\text{WO}_{4(\text{S})})$. Also, note that U.S. Nat. Bur. Stand. Circ. 500 [175] reported a value of -1652.680 kJ/mol for $\Delta H^\circ_{298.15\text{K}}(\text{Na}_2\text{WO}_{4(\text{S1})})$. This value was derived from the experimental heat of reaction of tungsten powder using an excess of Na_2O_2 . As mentioned in [170], this approach is most likely wrong owing to the possible formation of tungstate and complexes of peroxytungstate.

The standard enthalpy at 298.15 K of $\text{Na}_2\text{WO}_{4(\text{S1})}$ was estimated by us using the method proposed by Hisham and Benson [176]. These authors derived equations of the type $\frac{1}{a} \Delta H^\circ_{298.15\text{K}}(\text{M}_a\text{X}_b) = m \Delta H^\circ_{298.15\text{K}}(\text{MCl}) + \frac{1-m}{2} \Delta H^\circ_{298.15\text{K}}(\text{M}_2\text{O}) + \text{C}$, where m and C are two constants, and $\Delta H^\circ_{298.15\text{K}}$ refers to the standard enthalpy at 298.15 K of the corresponding solid compound. They selected the corresponding chloride and oxide of a metal M as reference compounds since, for the majority of metals, the chloride and oxide values are known with good accuracy. For the alkali tungstates, Hisham and Benson [176] obtained $m = 2.929$ and $\text{C} = -426.350$ kJ/mol. Using the $\Delta H^\circ_{298.15\text{K}}$ values for solid NaCl and Na_2O from the FactSage thermodynamic databases [42], $\Delta H^\circ_{298.15\text{K}}(\text{Na}_2\text{WO}_{4(\text{S1})})$ was assessed as -1,554,874 J/mol, which is reasonably close to the value recommended by JANAF [170] and selected in the present work. OQMD [128, 129] reported an enthalpy of formation at 0 K of -1,637,839 J/mol using DFT. The corresponding value given in Materials Project [130] is -1,500,057 J/mol.

Using calorimetry, King and Weller [171] performed low-temperature heat capacity measurements for $\text{Na}_2\text{WO}_{4(\text{S1})}$, and derived from them a value of 161.0840 J/mol.K for the standard entropy at

298.15 K ($S_{298.15\text{ K}}^\circ$). (The temperature range from 0 to 51 K was extrapolated using the Einstein and Debye functions.) This value, which is recommended by JANAF [170], was selected in the present work.

Na_2WO_4 was studied by Denielou et al. [115], using the same experimental technique that was previously discussed in detail for Na_2CrO_4 and Na_2MoO_4 . These authors provided fits (as a function of temperature) for their heat content measurements ($H_T - H_{273.15\text{ K}}$). For $\text{Na}_2\text{WO}_{4(\text{S1})}$, based on fourteen measurements between 345 and 849 K, $H_T - H_{273.15\text{ K}} = 8.047 \times 10^{-3}T^2 + 31.114T - 9,221 \text{ cal/mol}$ (0.4%, empirical standard variation of 8 calories). This fit was assumed to be valid from 298.15 K to our selected temperature of 861.5 K for the $\text{S}_1\text{-S}_2$ transition.

For $\text{Na}_2\text{WO}_{4(\text{S2})}$, based on nine measurements between 862 and 957 K, $H_T - H_{273.15\text{ K}} = 3.057 \times 10^{-2}T^2 - 7.104T + 14,520 \text{ cal/mol}$ (0.4%, empirical standard variation of 11 calories). This fit was assumed to be valid from 861.5 K until our selected temperature of fusion of 967.4 K.

For $\text{Na}_2\text{MoO}_{4(\text{L})}$, based on twelve measurements above 992 K, $H_T - H_{273.15\text{ K}} = 51.67 \times T - 7,076 \text{ cal/mol}$ (0.14%, empirical standard variation of 18 calories) [115].

In this work, the heat capacity expression (as a function of temperature) for Na_2WO_4 was selected in order to reproduce the heat content measurements ($H_T - H_{273.15\text{ K}}$) of Denielou et al. [115]. Calculations are compared to the available data in Figure 5.7. Also, the calculated heat capacity is shown along with the low-temperature measurements of King and Weller [171] in Figure 5.8. At room temperature, agreement is reasonable.

In Figure 5.7, the black full lines represent our final calculations while the red dashed line refers to $H_T - H_{273.15\text{ K}}$ heat contents obtained from the fit of the room temperature C_P data of [171] displayed in Figure 5.8. An average deviation of about 4 kJ/mol is calculated for the red dashed line, which is significantly higher than the experimental error of 33.5 J/mol reported by [115]. This lends support to our final calculations shown in Figures 5.7 and 5.8.

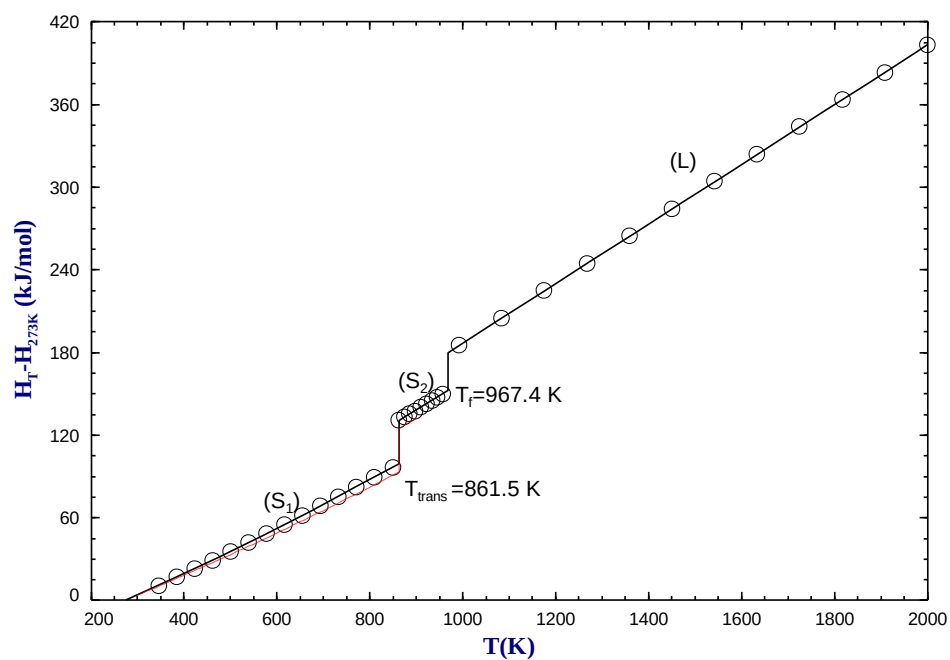


Figure 5.7 Calculated heat content $H_T - H_{273.15K}$ for Na_2WO_4 (enthalpies of transition are the weighted average of all available data presented in tables 5.23 and 5.25). Experimental data from [115] ($\circ$). Red dashed line : $H_T - H_{273.15K}$ fit of low-temperature heat capacity data shown in Figure 5.8.

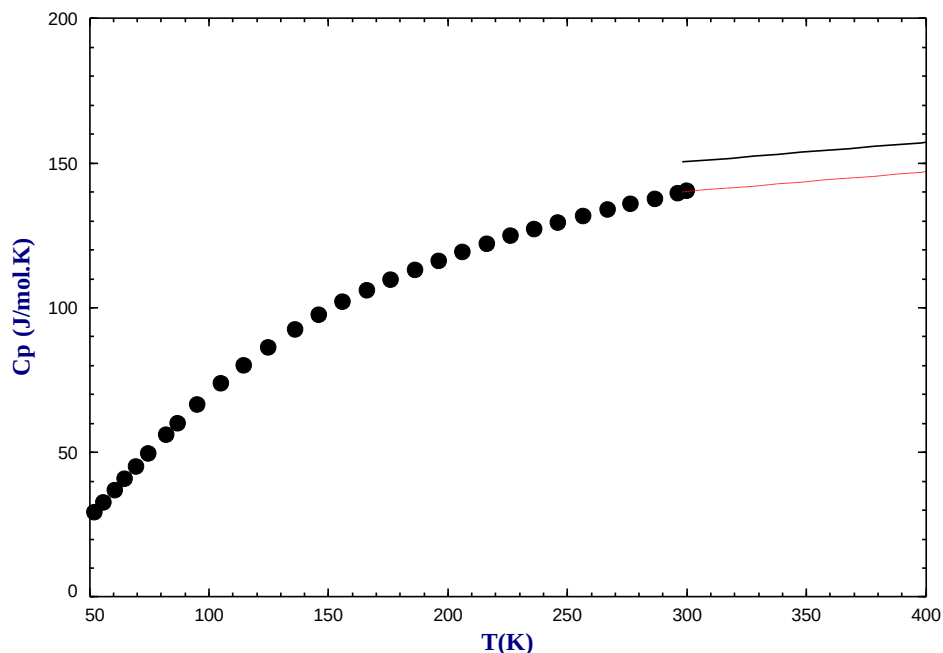


Figure 5.8 Calculated heat capacity at low temperatures for $\text{Na}_2\text{WO}_4(\text{s1})$. Experimental data from [171] (●). Red dashed line: best linear fit of room temperature C_p data.

5.4.6 Potassium tungstate

5.4.6.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transitions for K_2WO_4

The temperatures and enthalpy changes for the solid-solid transitions ($\text{S}_1\text{-S}_2$ and $\text{S}_2\text{-S}_3$) of K_2WO_4 were measured by DSC in the present work. These measurements along with all data from the literature are shown in Tables 5.28 and 5.29, respectively. Our experimental DSC thermogram is displayed in the Supporting Information (Figure B5). Some authors reported a single solid-solid transition [146, 177] while others reported two such transitions [103, 114, 151, 168]. Our DSC measurements at a heating/cooling rate of $10^\circ\text{C}/\text{min}$ confirmed that K_2WO_4 exhibits two different solid-solid transitions.

Table 5.28 Temperature and enthalpy change of transition S_1 - S_2 for K_2WO_4

$T_{\text{trans } S_1 \rightarrow S_2}$ (°C)	$\Delta H_{\text{trans } S_1 \rightarrow S_2}$ (kJ/mol)	Experimental Method	Reference
362.7	9.82	DSC (2 nd heating) 10°C/min	This work
361.7	9.84	DSC (3 rd heating) 10°C/min	This work
358	-	Cooling curves	[177]
350	9.121 ± 0.146	DTA 1°C/min	[146]
381	11.464	DTA	[114]
370	-	DTA 5°C/min	[151]
370	-	XRD*	[103]
-	12	Thermal analysis (DTA) 8-10°C/min	[168]
367.5	10.271	Weighted average of available data	This work

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

Table 5.29 Temperature and enthalpy change of transition S_2 - S_3 for K_2WO_4

$T_{\text{trans } S_2 \rightarrow S_3}$ (°C)	$\Delta H_{\text{trans } S_2 \rightarrow S_3}$ (kJ/mol)	Experimental Method	Reference
461.1	1.031	DSC (2 nd heating) 10°C/min	This work
461.3	1.001	DSC (3 rd heating) 10°C/min	This work
456	1.046	DTA	[114]
455	-	DTA 5°C/min	[151]
435	-	XRD*	[103]
-	1.2	Thermal analysis (DTA) 8-10°C/min	[168]
458.4	1.052	Weighted average of available data	This work

*A temperature focusing Guinier camera from Nonius was used with a calibrated thermocouple. The estimated error is about $\pm 10^\circ\text{C}$.

5.4.6.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for K_2WO_4

The properties of fusion (temperature and enthalpy change) were determined by [114, 123, 133, 146, 157, 178, 179]. All experimental data from the literature and our own DSC measurements are presented in Table 5.30.

Table 5.30 Temperature and enthalpy of fusion for K_2WO_4

$T_f \text{ } S_3 \rightarrow L$ (°C)	$\Delta H_f \text{ } S_3 \rightarrow L$ (kJ/mol)	Experimental Method	Reference
928.2	32.47	DSC (2 nd heating) 10°C/min	This work
927.7	32.57	DSC (3 rd heating) 10°C/min	This work
894	-	Cooling curves	[133]
926	-	Visual-polythermal analysis	[178]
926	-	Visual-polythermal analysis	[179]
928	31.087 ± 0.146	DTA 1°C/min	[146]
923	30.711	DTA	[114]
919	-	Visual-polythermal analysis	[123]
926	-	Thermal analysis	[157]
925.7	31.979	Weighted average of available data	This work

5.4.6.3 Recommended thermodynamic data for potassium tungstate K_2WO_4

Our selected thermodynamic data ($\Delta H_{298.15 \text{ K}}^\circ$, $S_{298.15 \text{ K}}^\circ$, and C_P) for potassium tungstate (K_2WO_4) are given in Table 5.31.

Table 5.31 Selected thermodynamic properties of K_2WO_4

Compound	T Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol)	$S_{298.15\text{ K}}^\circ$ (J/mol.K)	C_p (J/mol.K)
K_2WO_4 (S ₁)	298.15 to 640.6 (This work)	-1 581 600.0 (FactSage, SGPS database [42])	175.8080 (FactSage, SGPS database [42])	$113.39 + 0.12552T/K$ (FactSage, SGPS database [42])
K_2WO_4 (S ₂)	298.15 to 640.6 640.6 to 731.5 (This work)	-1 571 328.8 (This work)	191.8417 (This work)	$113.39 + 0.12552T/K$ (FactSage, SGPS database [42]) 194.556 (FactSage, SGPS database [42])
K_2WO_4 (S ₃)	298.15 to 640.6 640.6 to 1198.9 (This work)	-1 570 276.7 (This work)	193.2799 (This work)	$113.39 + 0.12552T/K$ (FactSage, SGPS database [42]) 194.556 (FactSage, SGPS database [42])
K_2WO_4 (L)	298.15 to 640.6 640.6 to 1198.9 1198.9 to 2000 (This work)	-1 538 298.0 (This work)	219.9533 (This work)	$113.39 + 0.12552T/K$ (FactSage, SGPS database [42]) 194.556 (FactSage, SGPS database [42]) 213.384 (FactSage, SGPS database [42])

For the temperature of the S₁-S₂ transition, the value reported by Nolte and Kordes [146] was discarded and, for the temperature of the S₂-S₃ transition, the value of Van Den Akker et al. [103] was not considered, since both values are relatively low compared to all other measurements (see Tables 5.28 and 5.29, respectively). Similarly, the melting temperature of Amadori [133] was ignored since it is lower than all other available data (see Table 5.30).

The standard enthalpy at 298.15 K ($\Delta H_{298.15\text{ K}}^\circ$) was taken directly from the SGPS database in FactSage [42]. Indeed, this value (-1,581.6 kJ/mol) is close to the value of -1,574.0 kJ/mol assessed using the equation of Hisham and Benson [176] with an approach similar to that described

previously for Na_2WO_4 . The validity of this equation was confirmed by us for the compounds Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 and K_2MoO_4 , for which there was good agreement between the estimated $\Delta H_{298.15\text{ K}}^\circ$ values and our selected values based on experimental data from the literature. For K_2WO_4 , OQMD [128, 129] reported an enthalpy of formation at 0 K of -1,645,268 J/mol using DFT. The corresponding value given in Materials Project [130] is -1,528,424 J/mol.

The standard entropy at 298.15 K ($S_{298.15\text{ K}}^\circ$) of $\text{K}_2\text{WO}_4(\text{s}_1)$ was taken directly from the SGPS database in FactSage [42] since no other values were available in the literature. Also, $S_{298.15\text{ K}}^\circ$ was roughly estimated from the exchange reactions $\text{Na}_2\text{WO}_4(\text{s}_1) + \text{K}_2\text{CrO}_4(\text{s}_1) \rightarrow \text{K}_2\text{WO}_4(\text{s}_1) + \text{Na}_2\text{CrO}_4(\text{s}_1)$ and $\text{Na}_2\text{WO}_4(\text{s}_1) + 2\text{KCl}(\text{s}) \rightarrow \text{K}_2\text{WO}_4(\text{s}_1) + 2\text{NaCl}(\text{s})$, for which ΔS was assumed to be null at 298.15 K. The corresponding estimates are 184.4640 J/mol.K and 181.9203 J/mol.K, respectively, which compares reasonably well to our selected value of 175.8080 J/mol.K.

To our knowledge, no experimental data for the heat capacity of K_2WO_4 are published. Therefore, the heat capacity expression (as a function of temperature) for this compound was taken directly from the SGPS database of FactSage [42].

5.5 Conclusions

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

The present work is the first step towards the development of a thermodynamic model for the Na^+ , $\text{K}^+ // \text{Cl}^-$, SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$, O^{2-} system that is relevant in the high temperature corrosion of equipment such as heat-transfer tubes. A critical evaluation of

the thermodynamic properties of the compounds $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{W}_2\text{O}_7$ and $\text{K}_2\text{W}_2\text{O}_7$ will be described in a subsequent paper. These compounds need to be considered since reactions of the type $2 \text{A}_2\text{MO}_4 = \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$ (where $\text{A} = \text{Na}, \text{K}$ and $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) may partly occur. Through phase equilibria calculations (which will avoid a tedious and costly trial and error experimental approach), the developed thermodynamic model will permit us to better understand high temperature corrosion phenomena in the temperature range 600-950°C. The developed thermodynamic model will also enable a better investigation of the chemistry of ash deposits and heat exchanger alloys since the combined ash/gas/alloy chemistry controls the melting behaviour of ashes.

5.6 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 apparatus, Ms. Evguenia Sokolenko for helping locate old articles and for translating them into English, Dr. Paul Lafaye for fruitful discussions, and Mr. Maxime Aubé for his helpful comments on the manuscript.

CHAPITRE 6 ARTICLE 2 : CRITICAL EVALUATION OF THE THERMODYNAMIC PROPERTIES OF $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{W}_2\text{O}_7$, and $\text{K}_2\text{W}_2\text{O}_7$

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Submitted for publication in Journal of Physical and Chemical Reference Data on April 14, 2023

Abstract: This study outlines an extensive investigation of crystallographic data and thermodynamic properties (including solid-solid transition and fusion) for sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sodium dimolybdate ($\text{Na}_2\text{Mo}_2\text{O}_7$), potassium dimolybdate ($\text{K}_2\text{Mo}_2\text{O}_7$), sodium ditungstate ($\text{Na}_2\text{W}_2\text{O}_7$), and potassium ditungstate ($\text{K}_2\text{W}_2\text{O}_7$). A thorough literature review was conducted to obtain a good understanding of the data available in the literature, and a critical and complete evaluation has been performed from room temperature to above the melting temperatures. This work is one of the key steps towards the development of a thermodynamic model for the Na^+ , K^+ // Cl^- , SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$, O^{2-} system, relevant for high temperature corrosion in atmospheres containing O-H-S-C-Cl and alkali salts.

6.1 Introduction

Combustion power plants and recovery boilers in the pulp and paper industry [25, 28, 36, 65] are mainly made of steels and stainless steels [16] with Ni, Cr, Mo, W and V as alloying elements [21, 22, 180]. Under operating conditions, these steel parts interact with oxygen, hydrogen, sulfur, carbon, chlorine, and alkaline salts (NaCl , KCl , Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3 , etc.). These various species are particularly aggressive and may lead to the formation of salt deposits. If the local temperature is high enough, a molten salt solution can form and be extremely corrosive. This

limits the durability of such installations and reduces their conversion efficiency. Moreover, conditions can lead to the solid oxide layers of the alloying elements (Cr, Mo, W, and V) complexing with the ions in solution to form dichromates, dimolybdates or ditungstates in the solid or liquid state, thus reducing the passivating layers and promoting further corrosion. As an example, at temperatures suitable for the combustion process, $\text{Na}_2\text{Cr}_2\text{O}_7(\text{L})$ (or $\text{K}_2\text{Cr}_2\text{O}_7(\text{L})$) can be formed when $\text{Cr}_2\text{O}_3(\text{S})$ interacts with $\text{NaCl}(\text{L})$ (or $\text{KCl}(\text{L})$) [70], resulting in the decrease of the protective properties of the oxide layer. In addition, $\text{K}_2\text{Cr}_2\text{O}_7$ may decrease the melting temperature through the formation of binary salt mixtures [29]. Similarly, in environments with a favorable oxygen potential, $\text{Na}_2\text{W}_2\text{O}_7(\text{S})$ may be formed due to the interaction of tungsten with Na [181].

In order to help our understanding of the corrosion phenomena, a thermodynamic model, as Gibbs energy functions of the different solid and liquid phases, for the Na^+ , K^+ // Cl^- , SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$, O^{2-} system is being developed. This requires as a first step the assessment of the thermodynamic properties (standard enthalpy of formation $\Delta H_{298.15\text{ K}}^\circ$ from the elements in their stable standard state at 298.15K and 1 atm, absolute (third law) entropy $S_{298.15\text{ K}}^\circ$ referenced at 298.15K and 1 atm, and heat capacity C_P as a function of temperature) of all relevant pure salts. In a previous paper [31], the thermodynamic properties and phase transitions for sodium and potassium chromates, molybdates, and tungstates were assessed using the available data from the literature and newly obtained DSC measurements. The present article is devoted to a similar assessment for the sodium and potassium dichromates, dimolybdates and ditungstates, which may be formed through reactions of the type $2\text{A}_2\text{MO}_4 = \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$ (where $\text{A} = \text{Na}, \text{K}$ and $\text{M} = \text{Cr}, \text{Mo}, \text{W}$). The crystal structures of those compounds were also taken into account in our literature search since this information is useful to identify possible solid solutions forming with other considered salts.

6.2 Crystal structures and space groups

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

Crystal structure information for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_{1,\text{S}2})$ is summarized in Table 6.1.

Table 6.1 Crystallographic data for polymorphs of $\text{Na}_2\text{Cr}_2\text{O}_7$

Allotrope of $\text{Na}_2\text{Cr}_2\text{O}_7$	Crystal structure	Space group	Reference
$\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S1})}$	Triclinic (stable below 246°C)	$P\bar{1}$	[182]
$\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S2})}$	Triclinic (stable from 246 to 356°C)	$A\bar{1}$	[182]

XRD analyses of Panagiotopoulos and Brown [182] revealed the presence of two allotropes for $\text{Na}_2\text{Cr}_2\text{O}_7$. The low-temperature form $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S1})}$ has a triclinic crystal structure with $P\bar{1}$ space group while the high-temperature allotrope $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S2})}$ has a triclinic crystal structure corresponding to $A\bar{1}$ space group. $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S2})}$ is formed by the displacement of two distinct layers (010) in $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S1})}$; these layers become equivalent in $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S2})}$ and the resulting high-temperature layer lies almost halfway between the two low-temperature layers [182].

Investigations trying to identify allotropic transformations of $\text{Na}_2\text{Cr}_2\text{O}_7$ are very contradictory. Indeed, thermal analyses between 70 and 300°C by Robinson et al [183] suggested no polymorphic transformations for $\text{Na}_2\text{Cr}_2\text{O}_7$. Afonskii [184] and Samuseva et al [185] reported a single allotropic phase transition at 240°C. Subsequent DTA analyses and high-temperature refractive index measurements conducted by Vesnin and Khripin [186] indicated the presence of four solid phases. Two of them were identified for the first time and their crystal structures were not specified [186].

In the present work, in agreement with the study of Panagiotopoulos and Brown [182], two different allotropes were introduced for $\text{Na}_2\text{Cr}_2\text{O}_7$. These allotropes have very similar crystal structures, and the corresponding transition may be a second-order transition. In the present work, this solid-solid transition was assumed to be a first-order transition, and the latent heat of transformation was estimated as 1,433 J/mol as will be discussed later. This is a reasonably low value.

Crystal structure information for $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S1,S2})}$ is summarized in Table 6.2.

Table 6.2 Crystallographic data for polymorphs of $K_2Cr_2O_7$

Allotrope of $K_2Cr_2O_7$	Crystal structure	Space group	Reference
$K_2Cr_2O_{7(S1)}$	Triclinic (stable below 258°C)	-	[187]
		$P\bar{1}$	[188]
		$C_i^1 - P\bar{1}$	[189]
		$P\bar{1}$	[190]
		$P\bar{1}$	[191]
$K_2Cr_2O_{7(S2)}$	Monoclinic (stable from 258 to 397°C)	-	[187]
		$C_{2h}^5 - P2_1/n$	[189]
		$P2_1/c$	[192]

In 1833, Mitscherlich [193] reported for the first time an allotropic transition for $K_2Cr_2O_7$ at about 250°C. Thereafter, several publications were devoted to the identification of the allotropic transitions and corresponding crystal structures. Jaffray and Labary [187] characterized three crystal forms using DTA, dilatometry and X-ray diffraction: a triclinic phase stable at room temperature, a monoclinic phase formed upon heating at about $269 \pm 2^\circ\text{C}$, and a metastable monoclinic phase formed from the high-temperature allotrope upon cooling below 240°C.

According to the XRD analysis of Jaffray and Labary, the three allotropes have different crystal structures. No supplementary information was provided and no investigations on single crystals were performed [187]. The metastable monoclinic form is known to be metastable at room temperature [187].

The refractometric and thermographic measurements of Vesnin and Khripin [186] led to solid-solid transition temperatures identical to those of Jaffray and Labary [187]. According to Vesnin and Khripin [186], the metastable form must be a low-temperature form of the high-temperature

(stable) monoclinic modification, and is thus identical to the monoclinic crystals precipitated from aqueous solutions [189].

According to Klement and Schwab [189], the phase transition from the low-temperature form to the high-temperature form is reversible, and the stable and metastable monoclinic forms reported by Jaffray and Labary [187] are identical since they have the same solubility in water. However, in the presence of moisture, the metastable form can quickly transform into the stable form, and it can always be associated with a small amount of the stable form although the solubility of these two forms can be very similar [186]. Moreover, other reversibility checks showed that, in both transformations (namely from the low-temperature form to the high-temperature form and vice-versa), the stratification lines of the crystals and therefore the orientation of the [100] axis, around which the crystal has rotated, have been preserved. Consequently, Klement and Schwab [189] claimed that the metastable form reported by Jaffray and Labary [187] does not exist.

The space group of the triclinic form at room temperature was determined by Rao using the statistical method of X-ray reflection intensity [188]. The intensity distribution curves showed a center of symmetry corresponding to the space group classification $P\bar{1}$. Further XRD analysis by Kuz'min et al [190], and by Brandon and Brown [191] have confirmed the same space group.

The high-temperature allotrope is monoclinic with the $C_{2h}^5 - P2_1/n$ space group, based on the XRD analysis of Klement and Schwab [189] and the electron diffraction analysis of Zhukova and Pinsker [192].

The exact crystal structure of the form obtained upon cooling of molten $K_2Cr_2O_7$ was not identified by Vesnin and Khripin [186], owing to the lack of data on the interplanar distances of the monoclinic modification at low temperatures [186].

In the present work, two different allotropes were finally introduced for $K_2Cr_2O_7$. Owing to contradictory information, the so-called metastable monoclinic form was not taken into account (Table 6.2).

Crystal structure information for $Na_2Mo_2O_7(S_1,S_2)$ is summarized in Table 6.3.

Table 6.3 Crystallographic data for polymorphs of $\text{Na}_2\text{Mo}_2\text{O}_7$

Allotrope of $\text{Na}_2\text{Mo}_2\text{O}_7$	Crystal structure	Space group	Reference
$\text{Na}_2\text{Mo}_2\text{O}_{7(\text{S1})}$	Orthorhombic (stable below 556°C)	Cmca D_{2h}^{18} *	[91]
		-	[93]
		Cmca D_{2h}^{18} *	[194]
$\text{Na}_2\text{Mo}_2\text{O}_{7(\text{S2})}$	Monoclinic (stable from 556 to 605°C)	-	[93]
		-	[194]

* The space group reported by the authors represents the abbreviated notation of the international tables of the 1935 edition (T. Hahn, U. Shmueli and J. W. Arthur, International tables for crystallography vol. 1: Reidel Dordrecht, 1983)

XRD analyses conducted by Lindqvist [91], Seleborg [195], Singh Mudher et al [93], and Saraiva et al. [194] have shown that $\text{Na}_2\text{Mo}_2\text{O}_7$ is orthorhombic at room temperature with the Cmca space group [91, 194, 195].

At high temperature, XRD analyses performed by Mudher et al [93] and Saraiva et al [194] revealed a monoclinic structure. However, no information was provided for the space group, and Mudher et al [93] reported that the symmetry of this phase has not yet been established.

Crystal structure information for $\text{K}_2\text{Mo}_2\text{O}_{7(\text{S1,S2})}$ is summarized in Table 6.4.

Table 6.4 Crystallographic data for polymorphs of $\text{K}_2\text{Mo}_2\text{O}_7$

Allotrope of $\text{K}_2\text{Mo}_2\text{O}_7$	Crystal structure	Space group	Reference
$\text{K}_2\text{Mo}_2\text{O}_{7(\text{S1})}$	Triclinic (stable below 519°C)	$P\bar{1}$ or P1	[196]
$\text{K}_2\text{Mo}_2\text{O}_{7(\text{S2})}$	Monoclinic (assumption) (stable from 519 to 549°C)	$P2_1/c$ or	This work

		$C_{2h}^5 - P2_1/n$ (assumption)	

The crystal structure of $K_2Mo_2O_7$ at room temperature was determined by XRD measurements performed by Magarill and Klevtsova [196]. A triclinic structure was obtained, with center of symmetry defined as $P\bar{1}$. Further refinement was performed using symmetry reduction in the $P1$ space group, but this had no significant effect on the results.

To this date, no information is available for the crystal structure and space group of $K_2Mo_2O_7$ at high temperatures. In the binary phase diagram $K_2Mo_2O_7$ - $K_2W_2O_7$, Amadori [133] reported at high temperatures a complete solid solution, thus indicating that the high-temperature allotropes (S_2) of $K_2Mo_2O_7$ and $K_2W_2O_7$ have very similar crystal structures. However, the crystal structure of $K_2W_2O_7$ is unknown. According to Amadori [133], the binary phase diagram $K_2Cr_2O_7$ - $K_2W_2O_7$ displays at high temperatures a complete solid solution. This suggests that both $K_2Mo_2O_{7(S2)}$ and $K_2W_2O_{7(S2)}$ have the same crystal structure as $K_2Cr_2O_{7(S2)}$ (that is, monoclinic with space group $P2_1/c$ or $C_{2h}^5 - P2_1/n$).

Crystal structure information for $Na_2W_2O_{7(S1,S2)}$ is summarized in Table 6.5.

Table 6.5 Crystallographic data for polymorphs of $Na_2W_2O_7$

Allotrope of $Na_2W_2O_7$	Crystal structure	Space group	Reference
$Na_2W_2O_{7(S1)}$	Orthorhombic (stable below 677°C)	Cmca	[110]
		Cmc2 ₁	[197]
$Na_2W_2O_{7(S2)}$	Monoclinic (assumption) (stable from 677 to 734°C)	-	This work

XRD analysis revealed that the crystal structure of $Na_2W_2O_7$ is isostructural to that of $Na_2Mo_2O_7$ [91]. According to Okada et al [110], the coordinates of atoms in $Na_2W_2O_7$ are very similar to those of $Na_2Mo_2O_7$, which were determined by Seleborg [195]. In addition, XRD analyses by Okada et

al [110] and Range and Haase [197] showed that $\text{Na}_2\text{W}_2\text{O}_7$ exhibits at room temperature an orthorhombic structure corresponding to the space group Cmca [110] or $\text{Cmc}2_1$ [197].

Using DTA, Nolte and Kordes [146] established that there are no solid-state phase transformations for this salt. On the other hand, according to the experimental binary phase diagrams $\text{Na}_2\text{Mo}_2\text{O}_7$ - $\text{Na}_2\text{W}_2\text{O}_7$ of Fedorov and Mokhosoev [198, 199] using the differential thermographic method (Kurnakov pyrometer), there is a continuous solid solution with a minimum at 90 mol% $\text{Na}_2\text{Mo}_2\text{O}_7$ and 590°C . This suggests the presence of a second allotrope for $\text{Na}_2\text{W}_2\text{O}_7$. Therefore, in the present work, two different allotropes were introduced for $\text{Na}_2\text{W}_2\text{O}_7$; $\text{Na}_2\text{W}_2\text{O}_{7(\text{S}2)}$ has the same crystal structure as monoclinic $\text{Na}_2\text{Mo}_2\text{O}_{7(\text{S}2)}$, whose space group remains unknown. The temperature for the solid-solid transition of $\text{Na}_2\text{W}_2\text{O}_7$ was estimated as 677°C , as will be discussed later.

Crystal structure information for $\text{K}_2\text{W}_2\text{O}_{7(\text{S}1,\text{S}2)}$ is summarized in Table 6.6.

Table 6.6 Crystallographic data for polymorphs of $\text{K}_2\text{W}_2\text{O}_7$

Allotrope of $\text{K}_2\text{W}_2\text{O}_7$	Crystal structure	Space group	Reference
$\text{K}_2\text{W}_2\text{O}_{7(\text{S}1)}$	Triclinic (assumption) (stable below 403°C)	$\text{P}\bar{1}$ (assumption)	This work
$\text{K}_2\text{W}_2\text{O}_{7(\text{S}2)}$	Monoclinic (assumption) (stable from 403 to 580°C)	$\text{P}2_1/\text{c}$ or $\text{C}_{2\text{h}}^5 - \text{P}2_1/\text{n}$ (assumption)	This work

To our knowledge, there is no information on the number of allotropes and crystal structure of solid $\text{K}_2\text{W}_2\text{O}_7$.

As discussed previously, $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{Mo}_2\text{O}_7$ both have two allotropes, and the two high-temperature forms have the same crystal structure as is already the case for the two low-temperature forms. According to the experimental binary phase diagram $\text{K}_2\text{W}_2\text{O}_7$ - $\text{K}_2\text{Cr}_2\text{O}_7$ of Amadori [133], there is a complete solid solution at high temperatures, which suggests that high-temperature $\text{K}_2\text{W}_2\text{O}_7$ has the same crystal structure as $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}2)}$ (that is, a monoclinic structure with $\text{P}2_1/\text{c}$ or $\text{C}_{2\text{h}}^5 - \text{P}2_1/\text{n}$ space group). Finally, two allotropes were considered for $\text{K}_2\text{W}_2\text{O}_7$ in the present

work, and the low-temperature form (S_1) was assumed to be triclinic with $P\bar{1}$ space group, by analogy with the low-temperature allotropes of $K_2Cr_2O_7$ and $K_2Mo_2O_7$. The temperature for the solid-solid transition of $K_2W_2O_7$ was assessed as 403°C, as will be explained later.

6.3 Selected thermodynamic properties

6.3.1 Sodium dichromate

6.3.1.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transition for $Na_2Cr_2O_7$

Table 6.7 lists all data from the literature corresponding to the temperature and enthalpy change for the solid-solid transition of $Na_2Cr_2O_7$.

Table 6.7 Temperature and enthalpy change of solid-solid transition for $Na_2Cr_2O_7$

$T_{trans} \ S_1 \rightarrow S_2$ (°C)	$\Delta H_{trans} \ S_1 \rightarrow S_2$ (kJ/mol)	Experimental Method	Reference
248	-	Thermal analysis (Heating curves) 5°C/min	[185]
240	-	DTA	[186] *
251	-	DSC 10°C/min	[200]
245.6	1.433 (see text)	Weighted average of available data	This work

*These authors reported four solid phases between room temperature and the melting temperature, with two other solid-solid transitions at 291°C and 330°C. The latter were not considered in this work.

6.3.1.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for $\text{Na}_2\text{Cr}_2\text{O}_7$

The measured values of the temperature and enthalpy of fusion of $\text{Na}_2\text{Cr}_2\text{O}_7$ collected from the literature are presented in Table 6.8.

Table 6.8 Temperature and enthalpy of fusion for $\text{Na}_2\text{Cr}_2\text{O}_7$

$T_f \text{ } S_2 \rightarrow L \text{ (}^\circ\text{C)}$	$\Delta H_f \text{ } S_2 \rightarrow L \text{ (kJ/mol)}$	Experimental Method	Reference
356.7 ± 1.0	-	Thermal analysis	[201]
360	-	Thermal analysis (Heating curves) 5°C/min	[185]
355.4	35.364	DSC 10°C/min	[200]
351.9	25.104	Value derived from heat contents measured by calorimetry	[202]
354	35.7 ± 0.75	DSC From 2 to 10°C/min	[203]
356.0	29.275	Weighted average of available data	This work

6.3.1.3 Recommended thermodynamic data for sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7$

Our selected thermodynamic data ($\Delta H_{298.15 \text{ K}}^\circ$, $S_{298.15 \text{ K}}^\circ$, and C_P) for sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7$ are provided in Table 6.9. For the pure liquid, below the temperature of fusion, the heat capacity (as a function of temperature) over a given temperature range was taken identical to that of the solid phase stable over this specific temperature range (i.e. C_P of the low-temperature allotrope (S_1) between 298.15 and 518.7 K, and C_P of the high-temperature allotrope (S_2) between 518.7 and 629.1 K). Similarly, for solid (S_2), below the temperature of the solid-solid transition, the heat capacity was taken identical to that of solid (S_1). For all three phases, the heat capacity above the

maximum temperature $T_{\max}$ of the highest temperature range in Table 6.9 is assumed to be constant and equal to the value of C_p at $T_{\max}$.

The same approach was used for all other compounds considered in this work. More details on the thermodynamic properties selected for $\text{Na}_2\text{Cr}_2\text{O}_7$ are given below.

Table 6.9 Selected thermodynamic properties of $\text{Na}_2\text{Cr}_2\text{O}_7$

Compound	T Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol) ^a	$S_{298.15\text{ K}}^\circ$ (J/mol.K) ^b	C_p (J/mol.K)
$\text{Na}_2\text{Cr}_2\text{O}_7$ (s1)	298.15 to 518.7 This work	-1 978 206.8 This work	251.3168 This work	267 This work
$\text{Na}_2\text{Cr}_2\text{O}_7$ (s2)	298.15 to 518.7 518.7 to 629.1 This work	-1 976 773.7 This work	254.0797 This work	267 This work 343.088 [202]
$\text{Na}_2\text{Cr}_2\text{O}_7$ (L)	298.15 to 518.7 518.7 to 629.1 629.1 to 2500 This work	-1 947 498.5 This work	300.6147 This work	267 This work 343.088 [202] 242.2042613 + 0.048116 T/K This work

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

^b Absolute (third law) entropy.

The data presented in Tables 6.7 and 6.8 are in good agreement. Our selected values of the temperatures for the solid-solid transition and fusion are the weighted average of all data found in the literature; the weighting was based on the expected accuracy of each experimental technique. The same methodology was applied for our selected value of the enthalpy of fusion. A similar approach was used for all other compounds investigated in this work.

Measurements of the enthalpy change for the solid-solid transition of $\text{Na}_2\text{Cr}_2\text{O}_7$ are not available in the literature. As a first approximation, the entropy change was assumed to be identical to that for $\text{K}_2\text{Cr}_2\text{O}_7$ (that is, 2.7628 J/mol.K based on the weighted average of the experimental measurements from [146, 186], as will be discussed later). This is the only compound of the type $\text{A}_2\text{M}_2\text{O}_7$ (with A = Na, K and M = Cr, Mo, W) for which the enthalpy change of the solid-solid transition was measured. The transition temperature has been evaluated as 518.7 K, which thus corresponds to an enthalpy change of about 1.433 kJ/mol. Note that this is a rough estimate since

the high-temperature allotropes of $\text{Na}_2\text{Cr}_2\text{O}_7$ (triclinic) and $\text{K}_2\text{Cr}_2\text{O}_7$ (monoclinic) do not have the same crystal structure.

The value of the standard enthalpy at 298.15 K ($\Delta H_{298.15\text{ K}}^\circ$) for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{s})$ was estimated as follows. The enthalpy of dissolution of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{s})$ ($\text{Na}_2\text{Cr}_2\text{O}_7(\text{s}) + 20\text{H}^+_{(\text{aq})} \rightarrow 2\text{Na}^+_{(\text{aq})} + 2\text{CrO}_4^{2-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$) was measured by calorimetry [126] as -89,412.1 J/mol. Values of $\Delta H_{298.15\text{ K}}^\circ(\text{Na}^+_{(\text{aq})})$, $\Delta H_{298.15\text{ K}}^\circ(\text{CrO}_4^{2-}_{(\text{aq})})$, $\Delta H_{298.15\text{ K}}^\circ(\text{OH}^-_{(\text{aq})})$, and $\Delta H_{298.15\text{ K}}^\circ(\text{H}_2\text{O}_{(\text{l})})$ were taken from the FactSage databases [42] as -239,731 J/mol, -881,150.4 J/mol, -229,987.0 J/mol, and -285,830 J/mol, respectively.

The standard enthalpy at 298.15 K of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{s})$ was estimated by us using the method proposed by Hisham and Benson [176]. These authors derived equations of the type $\frac{1}{a}\Delta H_{298.15\text{ K}}^\circ(\text{M}_a\text{X}_b) = m\Delta H_{298.15\text{ K}}^\circ(\text{MCl}) + \frac{1-m}{2}\Delta H_{298.15\text{ K}}^\circ(\text{M}_2\text{O}) + \text{C}$, where m and C are two constants, and $\Delta H_{298.15\text{ K}}^\circ$ refers to the standard enthalpy at 298.15 K of the corresponding solid compound. They selected the corresponding chloride and oxide of a metal M as reference compounds since, for the majority of metals, the chloride and oxide values are known with good accuracy. For alkali dichromates, Hisham and Benson [176] obtained $m = 1.3$ and $\text{C} = -516.724$ kJ/mol. Using the $\Delta H_{298.15\text{ K}}^\circ$ values for NaCl and Na_2O from the FactSage thermodynamic databases [42], $\Delta H_{298.15\text{ K}}^\circ(\text{Na}_2\text{Cr}_2\text{O}_7(\text{s}))$ was estimated as -1,976,965 J/mol, which is very close to the value of -1,978,207 J/mol selected in the present work and derived from the calorimetric measurements of Nelson et al [126]. The Open Quantum Materials Database (OQMD) reported an enthalpy of formation at 0 K of -1,944,372 J/mol derived from Density Functional Theory (DFT) calculations [128, 129]. The corresponding value given in Materials Project [130] is -1,970,906 J/mol.

Owing to the lack of data, as a first approximation, the standard entropy at 298.15 K ($S_{298.15\text{ K}}^\circ$) of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{s})$ was assessed as 251.3168 J/mol.K from the exchange reaction $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}) + \text{K}_2\text{Cr}_2\text{O}_7(\text{s}) \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7(\text{s}) + \text{K}_2\text{Mo}_2\text{O}_7(\text{s})$, for which $\Delta S = 0$ was assumed at 298.15 K. The $S_{298.15\text{ K}}^\circ$ values for $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s})$, $\text{K}_2\text{Cr}_2\text{O}_7(\text{s})$ and $\text{K}_2\text{Mo}_2\text{O}_7(\text{s})$ selected in the present work will be discussed later.

Dellien et al [204] assessed a $S_{298.15\text{ K}}^\circ$ value of 267.776 J/mol.K for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_1)$. This estimate was not considered in this work since the methodology was not described.

The heat capacity of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_2)$ was derived from the heat content measurements ($H_T - H_{298.15\text{ K}}$) of Nguyen-Duy and Dancy [202] obtained by drop calorimetry over a limited temperature range (from 521 to 604 K), and was assumed to be valid from our selected temperature of 518.7 K for the S_1 - S_2 transition to our selected temperature of fusion of 629.1 K. The heat content measurements of the same authors for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{L})$ between 629 and 654 K (i.e. a very limited temperature range) were discarded since they most likely correspond to much too high heat capacity values. Indeed, in the same study, Nguyen-Duy and Dancy [202] derived a C_p of 213.384 J/mol.K for $\text{NaNO}_3(\text{L})$ between 579 and 620 K. This is much higher than the value of 138.2 J/mol.K recommended above 579 K by Robelin et al [205], based on a critical evaluation of all available data from the literature (see Figure 6.1). Finally, in the present work, the heat capacity of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{L})$ above the melting temperature was taken as the average of the heat capacities of $\text{Na}_2\text{S}_2\text{O}_7(\text{L})$ [39], $\text{Na}_2\text{Mo}_2\text{O}_7(\text{L})$ and $\text{Na}_2\text{W}_2\text{O}_7(\text{L})$ (The heat capacities of the latter compounds will be discussed later.) This is a reasonable assumption since the heat capacities of $\text{Na}_2\text{SO}_4(\text{L})$ [39], $\text{Na}_2\text{CrO}_4(\text{L})$ [31], $\text{Na}_2\text{MoO}_4(\text{L})$ [31] and $\text{Na}_2\text{WO}_4(\text{L})$ [31] are very similar.

The heat capacity of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_1)$ was assumed to be constant by analogy with $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_2)$, and was set to 267.0 J/mol.K to reproduce satisfactorily the heat content data of Nguyen-Duy and Dancy [202] for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_2)$ (see Figure 6.2). (The enthalpy change for the S_1 - S_2 transition was evaluated previously.) As seen in Table 6.9, the heat capacity selected for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_2)$ is significantly higher than that of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_1)$. It may be somewhat too large since it was derived from the heat content measurements of Nguyen-Duy and Dancy [202], which were very doubtful for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{L})$. However, based on the comparison between the data of the same authors for $\text{NaNO}_3(\text{S}_2)$ and the calculations from reference [205] (see Figure 6.1), it was not possible to derive a correction that could have been applied to the original heat content measurements for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_2)$.

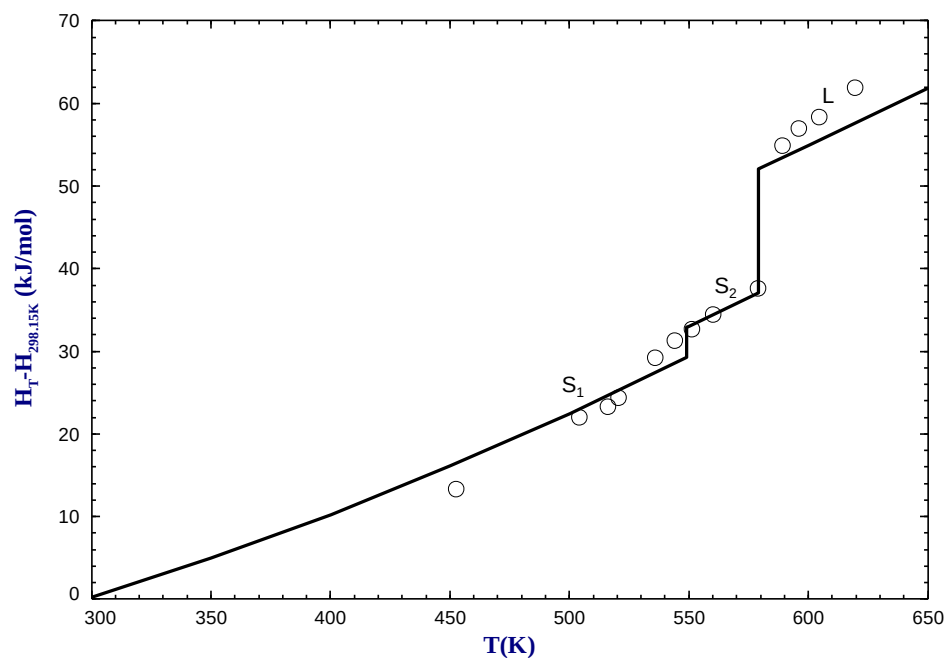


Figure 6.1 Calculated heat content $H_T - H_{298.15K}$ for NaNO_3 . Experimental data from [202] (○) and full lines calculated from [205].

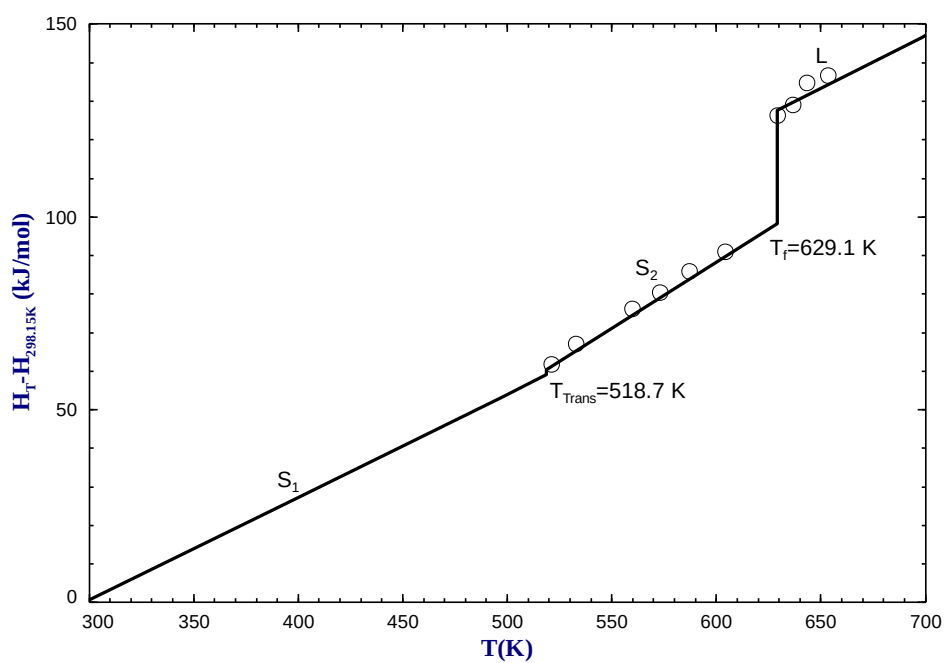


Figure 6.2 Calculated heat content $H_T - H_{298.15K}$ for $\text{Na}_2\text{Cr}_2\text{O}_7$. Experimental data from [202] (○).

Calculated values of $H_T - H_{298.15K}$ for $\text{Na}_2\text{Cr}_2\text{O}_7$ are shown along with the available measurements in Figure 6.2.

6.3.2 Potassium dichromate

6.3.2.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transition for $\text{K}_2\text{Cr}_2\text{O}_7$

Table 6.10 presents all data from the literature corresponding to the temperature and enthalpy change for the solid-solid transition of $\text{K}_2\text{Cr}_2\text{O}_7$.

Table 6.10 Temperature and enthalpy change of solid-solid transition for $\text{K}_2\text{Cr}_2\text{O}_7$

$T_{\text{trans}} \text{ } S_1 \rightarrow S_2$ (°C)	$\Delta H_{\text{trans}} \text{ } S_1 \rightarrow S_2$ (kJ/mol)	Experimental Method	Reference
236	-	Cooling curves with automatic recording; microscopic study of solidified melt sections	[132]
236.8 ± 0.5	-	Platinum resistance thermometer coupled with a Callendar and Griffiths bridge and a Hartmann and Braun moving coil galvanometer	[183]
241.6 ± 1	-	Thermal analysis	[201]
269 ± 2 $255 \pm 2^*$	-	DTA	[187]
264 ± 5	-	Thermal analysis, using hot stage microscopy (HSM)	[189]

269 ± 2	-	Electron diffraction	[192]
270	1.723	Heating curves	[186] ** ΔH_f is taken from reference 4
241.6	2033 (discarded : see text)	-	[137]
264	1.213	DTA 1°C/min	[146]
269	-	Raman spectroscopy	[206]
268	-	DSC 10°C/min	[200]
258.3	1.468	Weighted average of available data	This work

* This temperature was measured when the same product was heated anew.

** These authors reported four solid phases between room temperature and the melting temperature, with two other solid-solid transitions at 345°C and 380°C (enthalpy changes of 0.03 and 0.18 cal/g, respectively). Those two transitions were not considered in this work.

6.3.2.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for $K_2Cr_2O_7$

The properties of fusion (temperature and enthalpy change) were measured by [131, 132, 137, 146, 183, 186, 187, 200, 202, 203, 206-210]. The heat of fusion was measured by drop calorimetry [202], DTA [146], and DSC [200, 203]. All experimental data from the literature are gathered in Table 6.11.

Table 6.11 Temperature and enthalpy of fusion for $K_2Cr_2O_7$

T_f $S_2 \rightarrow L$ (°C)	ΔH_f $S_2 \rightarrow L$ (kJ/mol)	Experimental Method	Reference
400	-	Heating curves with visual reading	[131]
395	-	Cooling curves with automatic recording; microscopic study of solidified melt sections	[132]
397.5 ± 0.5	-	Melting curves	[207]
398.4	-	Platinum resistance thermometer coupled with a Callendar and Griffiths bridge and a Hartmann and Braun moving coil galvanometer	[183]
398	-	DTA	[187]
398	36.694	Heating curves	[186]
398	36.7	Recommended value in the compilation	[137]
400	37.279	DTA 1°C/min	[146]
400	-	DTA	[208]
398	-	Raman spectroscopy	[206]

394	-	Cooling curves 5°C/min	[209]
400	-	DTA	[210]
392.9	39.330	Value derived from heat contents measured by calorimetry	[202]
395.2	40.389	DSC 10°C/min	[200]
394	40.07 ± 0.4	DSC From 2 to 10°C/min	[203]
397.5	39.044	Weighted average of available data	This work

6.3.2.3 Recommended thermodynamic data for potassium dichromate $K_2Cr_2O_7$

Our selected thermodynamic data ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_p) for potassium dichromate $K_2Cr_2O_7$ are given in Table 6.12.

Table 6.12 Selected thermodynamic properties of $K_2Cr_2O_7$

Compound	T Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol)	$S_{298.15\text{ K}}^\circ$ (J/mol.K)	C_p (J/mol.K)
$K_2Cr_2O_7$ (s1)	298.15 to 531.5 This work	-2 060 377.2 This work	291.2064 [150]	219.657 This work
$K_2Cr_2O_7$ (s2)	298.15 to 531.5 531.5 to 670.6 This work 670.6 to 2000* This work	-2 058 909.0 This work	293.9690 This work	219.657 This work 401.664 [202] 207.041636 + 0.1033046 T/K - 436000 (T/K) ⁻²
$K_2Cr_2O_7$ (L)	298.15 to 531.5	-2 019 865.1	352.1911	219.657 This work

	531.5 to 670.6 670.6 to 2000 This work	This work	This work	401.664 [202] 207.041636 + 0.1033046 T/K - 436000 (T/K) ⁻²

* : Above the temperature of fusion, the heat capacity of $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}2)}$ was assumed to be equal to that of $\text{K}_2\text{Cr}_2\text{O}_{7(\text{L})}$ to ensure a reasonable extrapolation of the Gibbs energy at high temperatures. In absence of this additional C_p range, the high-temperature allotrope would be calculated to be more stable than the pure liquid above 2096 K.

Most of the data in Tables 6.10 and 6.11 are in good agreement. Therefore, the temperatures and enthalpy changes for the solid-solid transition and fusion were evaluated and weighted with respect to the set of data found in the literature. Note that the unreasonable enthalpy change of 2033 kJ/mol reported by Lax [137] for the solid-solid transition was discarded; this may very well be a typo. Also, the experimental technique used by this author was not described.

Owing to the lack of data, the standard enthalpy at 298.15 K ($\Delta H_{298.15\text{ K}}^\circ$) of $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}1)}$ was estimated as -2,060,377.2 J/mol using the equation of Hisham and Benson [176] with an approach similar to that described previously for $\text{Na}_2\text{Cr}_2\text{O}_7$. This estimate is expected to be reliable since very good agreement was observed for $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S}1)}$ between the estimated $\Delta H_{298.15\text{ K}}^\circ$ value and our selected value based on experimental data from the literature. For $\text{K}_2\text{Cr}_2\text{O}_7$, Materials Project reported [130] an enthalpy of formation at 0 K of -2,049,445 J/mol using DFT, whereas OQMD [128, 129] reported a value of -2,005,930 J/mol (for the C2/c space group).

The standard entropy at 298.15 K ($S_{298.15\text{ K}}^\circ$) of $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}1)}$ was derived by Popov and Kolesov [150] as 291.2064 J/mol.K by integration of their experimental C_p values from 60 to 300 K obtained by calorimetry. Lax [137] reported a value of 291.2 J/mol.K, which might be directly taken from [150]. The value of Popov and Kolesov [150] was selected in the present work.

The heat capacity of $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}2)}$ was derived from the heat content measurements ($H_T - H_{298.15\text{ K}}$) of Nguyen-Duy and Dancy [202] obtained by drop calorimetry over a limited temperature range (from 536 to 639 K), and was assumed to be valid from our selected temperature of 531.5 K for

the S_1 - S_2 transition to our selected temperature of fusion of 670.6 K. The heat content measurements of the same authors for $K_2Cr_2O_{7(L)}$ between 681 and 706 K (i.e. a very limited temperature range) were not considered since they most likely correspond to much too high heat capacity values. Indeed, in the same article, Nguyen-Duy and Dancy [202] derived a C_p of 234.304 J/mol.K for $KNO_{3(L)}$ between 518 and 616 K. This is substantially higher than the value of 142.7 J/mol.K recommended above 606 K by Robelin et al [205], based again on a critical evaluation of all available data from the literature (see Figure 6.3). Finally, in this work, the heat capacity of $K_2Cr_2O_{7(L)}$ above the melting temperature was taken as the average of the heat capacities of $K_2S_2O_{7(L)}$ [39], $K_2Mo_2O_{7(L)}$ and $K_2W_2O_{7(L)}$. (The heat capacities of the latter compounds will be discussed later.) This is a reasonable assumption since the heat capacities of $K_2SO_{4(L)}$ [39], $K_2CrO_{4(L)}$ [31], $K_2MoO_{4(L)}$ [31] and $K_2WO_{4(L)}$ [31] are close to each other.

The heat capacity of $K_2Cr_2O_{7(S1)}$ was assumed to be constant by analogy with $K_2Cr_2O_{7(S2)}$, and was set to 219.657 J/mol.K in order to reproduce satisfactorily the room temperature C_p value of Popov and Kolesov [150] (see Figure 6.5) and the heat content data of Nguyen-Duy and Dancy [202] for $K_2Cr_2O_{7(S2)}$ (see Figure 6.4). (The enthalpy change for the S_1 - S_2 transition was evaluated previously.) As seen in Table 6.12, the heat capacity selected for $K_2Cr_2O_{7(S2)}$ is substantially higher than that of $K_2Cr_2O_{7(S1)}$. It may very well be too large since it was derived from the heat content measurements of Nguyen-Duy and Dancy [202], which were very questionable for $K_2Cr_2O_{7(L)}$. Nevertheless, based on the comparison between the data of the same authors for $KNO_{3(S2)}$ and the calculations from reference [205] (see Figure 6.3), it was not possible to derive a correction that could have been applied to the heat content measurements for $K_2Cr_2O_{7(S2)}$.

Calculated values of $H_T - H_{298.15K}$ are compared to the available measurements in Figure 6.4. The calculated heat capacity at low temperatures for $K_2Cr_2O_{7(S1)}$ is shown in Figure 6.5 along with the data of Popov and Kolesov [150] and the two series of data obtained by Nan et al [211] using adiabatic calorimetry over the temperature range of 80-390 K.

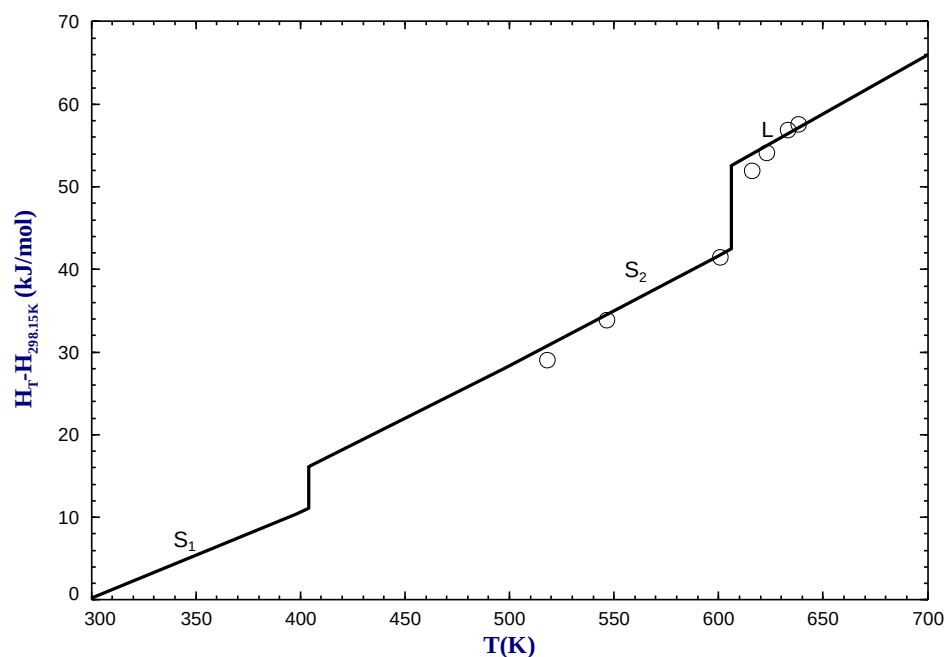


Figure 6.3 Calculated heat content $H_T - H_{298.15K}$ for KNO_3 . Experimental data from [202]

($\circ$) and full lines calculated from [205].

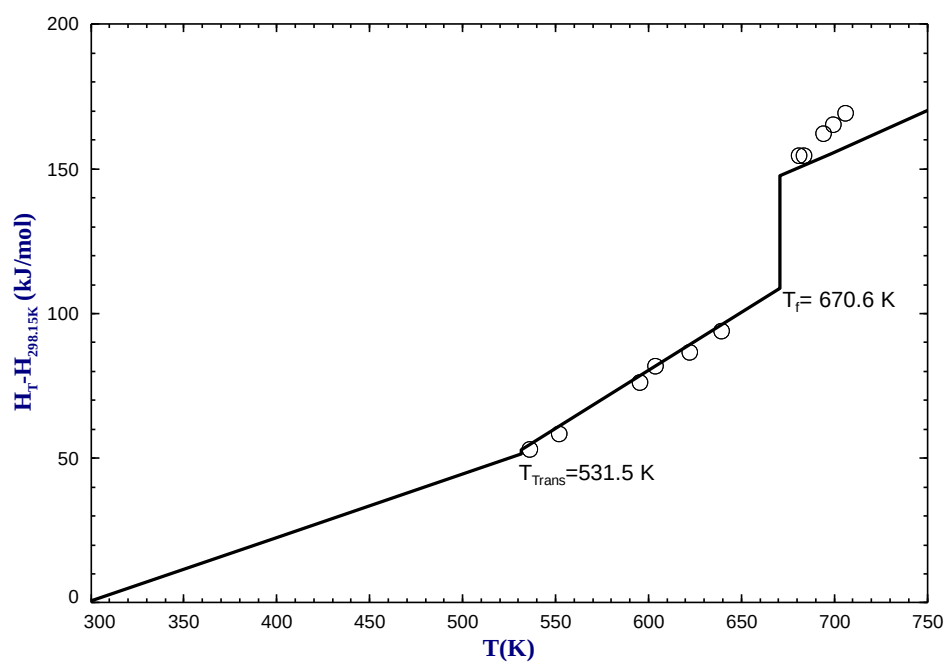


Figure 6.4 Calculated heat content $H_T - H_{298.15K}$ for $K_2Cr_2O_7$. Experimental data from [202] ($\circ$).

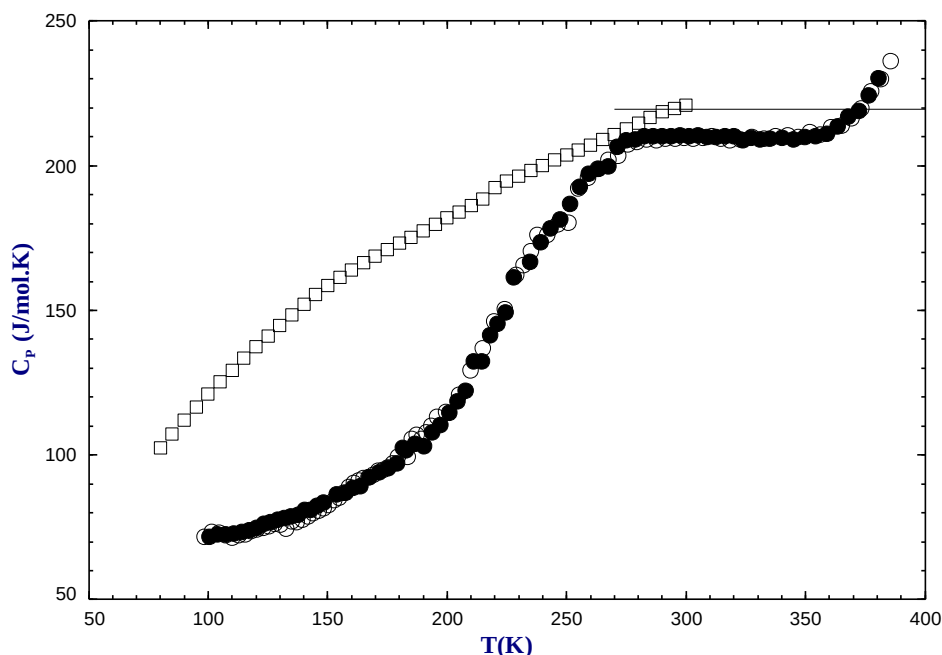


Figure 6.5 Calculated heat capacity at low temperatures for $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}1)}$. Experimental data from [150] ($\square$), and [211] ($\circ$ and $\bullet$).

6.3.3 Sodium dimolybdate

6.3.3.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transition for $\text{Na}_2\text{Mo}_2\text{O}_7$

Table 6.13 presents all data from the literature corresponding to the temperature and enthalpy change for the solid-solid transition of $\text{Na}_2\text{Mo}_2\text{O}_7$. Owing to the lack of relevant data, the enthalpy change was estimated as will be discussed later.

Table 6.13 Temperature and enthalpy change of solid-solid transition for $\text{Na}_2\text{Mo}_2\text{O}_7$

$T_{\text{trans}} \text{ } S_1 \rightarrow S_2$ ($^{\circ}\text{C}$)	$\Delta H_{\text{trans}} \text{ } S_1 \rightarrow S_2$ (kJ/mol)	Experimental Method	Reference
556.9	-	DSC 10 $^{\circ}\text{C}/\text{min}$	[93]
554.9	-	DTA	

		10°C/min	
555.9	2.290 (see text)	Weighted average of available data	This work

6.3.3.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for $\text{Na}_2\text{Mo}_2\text{O}_7$

The properties of fusion (temperature and enthalpy change) of $\text{Na}_2\text{Mo}_2\text{O}_7$ collected from the literature are listed in Table 6.14. Owing to the lack of relevant data, the enthalpy of fusion was assessed as will be explained later.

Table 6.14 Temperature and enthalpy of fusion for $\text{Na}_2\text{Mo}_2\text{O}_7$

$T_f \text{ } S_2 \rightarrow L \text{ (}^\circ\text{C)}$	$\Delta H_f \text{ } S_2 \rightarrow L \text{ (kJ/mol)}$	Experimental Method	Reference
612	-	Differential thermographic (Kurnakov pyrometer) 10°C/min	[198]
602.9 ± 5	-	Drop method using Calvet high temperature calorimeter	[152]
599.9	-	DSC 10°C/min	[93]
605.5	83.193 (see text)	Weighted average of available data	This work

6.3.3.3 Recommended thermodynamic data for sodium dimolybdate $\text{Na}_2\text{Mo}_2\text{O}_7$

Our selected thermodynamic data ($\Delta H_{298.15 \text{ K}}^\circ$, $S_{298.15 \text{ K}}^\circ$, and C_p) for sodium dimolybdate $\text{Na}_2\text{Mo}_2\text{O}_7$ are presented in Table 6.15.

Table 6.15 Selected thermodynamic properties of $\text{Na}_2\text{Mo}_2\text{O}_7$

Compound	T Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol)	$S_{298.15\text{ K}}^\circ$ (J/mol.K)	C_p (J/mol.K)
$\text{Na}_2\text{Mo}_2\text{O}_7$ (S1)	298.15 to 829 This work	-2 243 980.3 This work	250.6216 [212]	173.636 + 0.144348 T/K [213]
$\text{Na}_2\text{Mo}_2\text{O}_7$ (S2)	298.15 to 878.6 This work	-2 241 690.0 This work	253.3843 This work	173.636 + 0.144348 T/K [213]
$\text{Na}_2\text{Mo}_2\text{O}_7$ (L)	298.15 to 2000 This work	-2 158 496.8 This work	348.0727 This work	173.636 + 0.144348 T/K [213]

The data in Tables 6.13 and 6.14 are consistent with each other.

To our knowledge, measurements of the enthalpy change for the solid-solid transition and fusion of $\text{Na}_2\text{Mo}_2\text{O}_7$ are not available in the literature. As a first approximation, the entropy change for the solid-solid transition was assumed to be identical to that for $\text{K}_2\text{Cr}_2\text{O}_7$ (that is, 2.7628 J/mol.K based on the weighted average of the experimental measurements from [146, 186]). The transition temperature for $\text{Na}_2\text{Mo}_2\text{O}_7$ has been evaluated as 829 K, which thus corresponds to an enthalpy change of about 2.290 kJ/mol. Note that this is a rough estimate since the low-temperature allotropes of $\text{Na}_2\text{Mo}_2\text{O}_7$ (orthorhombic) and $\text{K}_2\text{Cr}_2\text{O}_7$ (triclinic) do not have the same crystal structure.

The entropy of fusion of $\text{Na}_2\text{Mo}_2\text{O}_7$ was assumed to be identical to that of $\text{Na}_2\text{W}_2\text{O}_7$ (that is, 94.6845 J/mol.K as will be discussed later). This is a reasonable assumption since the two allotropes $\text{Na}_2\text{Mo}_2\text{O}_7$ (S2) and $\text{Na}_2\text{W}_2\text{O}_7$ (S2) have the same crystal structure (with an undefined space group), the same alkali cation (Na^+) and very similar radii for the other cations ($\text{Mo}^{6+} = 0.59 \text{ \AA}$ and $\text{W}^{6+} = 0.60 \text{ \AA}$ in an octahedral geometry) [214]. The temperature of fusion of $\text{Na}_2\text{Mo}_2\text{O}_7$ has been estimated as 878.6 K, which thus corresponds to an enthalpy of fusion of about 83.193 kJ/mol.

Using a cycle of calorimetric reactions, Koehler et al [160] evaluated the standard enthalpy at 298.15 K of $\text{Na}_2\text{Mo}_2\text{O}_7$ (S1) as -2,244,297 J/mol. The molar enthalpy of dissolution of $\text{Na}_2\text{Mo}_2\text{O}_7$ in

a NaOH solution was measured at 298.15 K by Tangri et al [158] using an isoperibol calorimeter. The molar enthalpy of solution at infinite dilution was measured as -55.89 ± 0.69 kJ/mol [158], and a standard enthalpy at 298.15 K of $-2,245.02 \pm 0.81$ kJ/mol was then derived for $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_1)$. Using the same experimental technique, Suponitskii et al [215] obtained $\Delta H_{298.15\text{ K}}^\circ = -2,242,624$ J/mol. Mathews et al [216] performed electromotive force (EMF) measurements for the high temperature galvanic cell $\text{Pt, Ar} + \text{CO}_2 + \text{O}_2, \text{Na}_2\text{CO}_3 | \text{NASICON} | \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{MoO}_4, \text{O}_2 + \text{CO}_2 + \text{Ar, Pt}$ over the temperature range 650-800 K (where NASICON is a material for electrodes used in electrochemical cells). The cell reaction is $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}) + \text{Na}_2\text{CO}_3(\text{s}) = 2 \text{Na}_2\text{MoO}_4(\text{s}) + \text{CO}_2(\text{g})$, and the authors reported the Gibbs energy change $\Delta G^\circ = 53.78 - 0.160T$ kJ/mol (± 1 kJ) for this reaction. The calculated Gibbs energy change of the cell reaction is compared to the data points of Mathews et al [216] in Figure 6.6. In this figure, the two vertical dashed lines correspond to the solid-solid transitions $\text{Na}_2\text{MoO}_4(\text{s}_1) = \text{Na}_2\text{MoO}_4(\text{s}_2)$ and $\text{Na}_2\text{CO}_3(\text{s}_2) = \text{Na}_2\text{CO}_3(\text{s}_3)$, respectively.

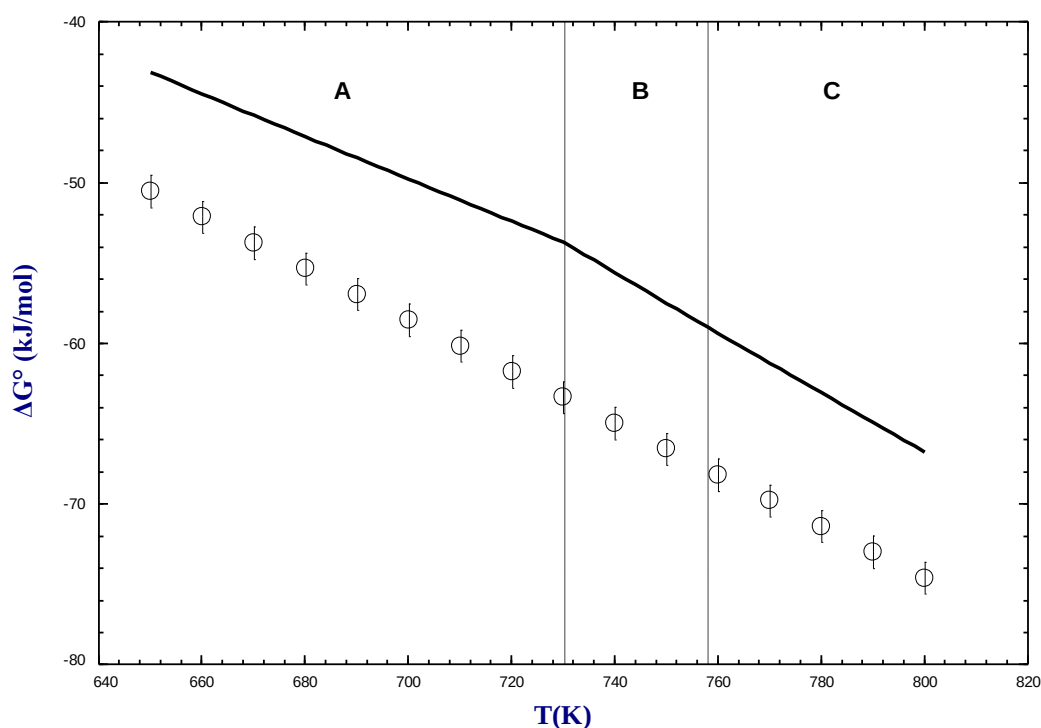


Figure 6.6 Calculated Gibbs energy change ΔG° for the cell reaction investigated by Mathews et al [216]. Experimental data from [216] ($\bigcirc$). A: $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_1) + \text{Na}_2\text{CO}_3(\text{s}_2) = 2 \text{Na}_2\text{MoO}_4(\text{s}_1) + \text{CO}_2(\text{g})$; B : $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_1) + \text{Na}_2\text{CO}_3(\text{s}_2) = 2 \text{Na}_2\text{MoO}_4(\text{s}_2) + \text{CO}_2(\text{g})$; C : $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_1) + \text{Na}_2\text{CO}_3(\text{s}_3) = 2 \text{Na}_2\text{MoO}_4(\text{s}_2) + \text{CO}_2(\text{g})$.

The calculated Gibbs energy change of the cell reaction investigated by Mathews et al [216] overestimates the measurements of these authors by about 9 kJ/mol, which is somewhat outside the reported experimental error limit. The thermodynamic properties ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_P) selected for $\text{Na}_2\text{Mo}_2\text{O}_7(\text{S}_1)$ in the present study were all based on experimental data from the literature. Also, the thermodynamic properties of Na_2CO_3 were critically reviewed by Lindberg et al [41] while those of both allotropes of Na_2MoO_4 were based on our careful evaluation of all experimental data from the literature [31]. For all these reasons, it is believed that the calculations shown in Figure 6.6 have a reasonable accuracy.

Since the $\Delta H_{298.15\text{ K}}^\circ$ values given by Koehler et al [160], Tangri et al [158] and Suponitskii et al [215] are close to each other, their average was selected in the present work. The obtained value (-2,243,980.3 J/mol) is very close to the value of -2,244,246 J/mol estimated using the equation of Hisham and Benson [176] (for alkali dimolybdates, $m = 0.980$ and $C = -715.046$ kJ/mol). OQMD[128, 129] reported an enthalpy of formation at 0 K of -2,393,319 J/mol using DFT calculations. The corresponding value given in Materials Project [130] is -2,238,363 J/mol.

For the standard entropy at 298.15 K ($S_{298.15\text{ K}}^\circ$) of $\text{Na}_2\text{Mo}_2\text{O}_7(\text{S}_1)$, Weller and Kelley [212] reported a value of 250.6216 ± 2.092 J/mol.K, assessed by integration of their low-temperature heat capacity measurements obtained by calorimetry. The Einstein and Debye functions were used over the extrapolated temperature range of 0K to 51K.

To our knowledge, no direct high-temperature C_P measurements are available in the literature. Therefore, the expression of the heat capacity as a function of temperature was directly taken from the SGPS database available in FactSage [42] (validity from 298.15K to 888K) and was assumed to be valid for all phases (S_1 , S_2 and liquid).

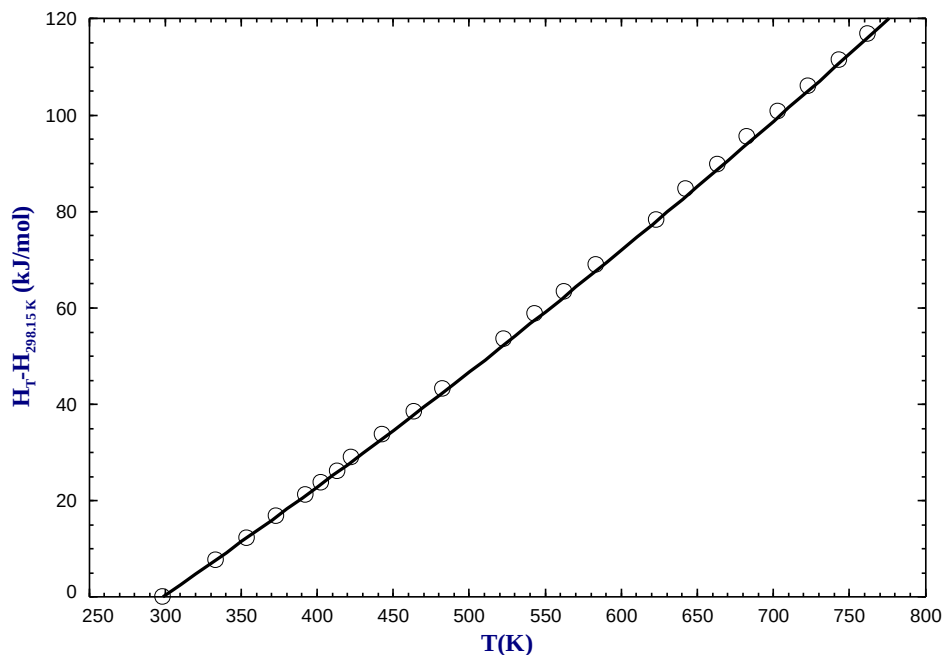


Figure 6.7 Calculated heat content $H_T - H_{298.15 K}$ for $\text{Na}_2\text{Mo}_2\text{O}_7(\text{S1})$. Experimental data from [152] (○).

Calculated values of $H_T - H_{298.15 K}$ are shown along with the data of Iyer et al [152] in Figure 6.7. These data were obtained between 335 K and 760 K using drop calorimetry in a high temperature Calvet calorimeter. The DTA study of the same authors from 298.15 K to about 881 K revealed no solid-solid transition.

The calculated heat capacity at low temperatures for $\text{Na}_2\text{Mo}_2\text{O}_7(\text{S1})$ is shown in Figure 6.8 along with the measurements of Weller and Kelley [212].

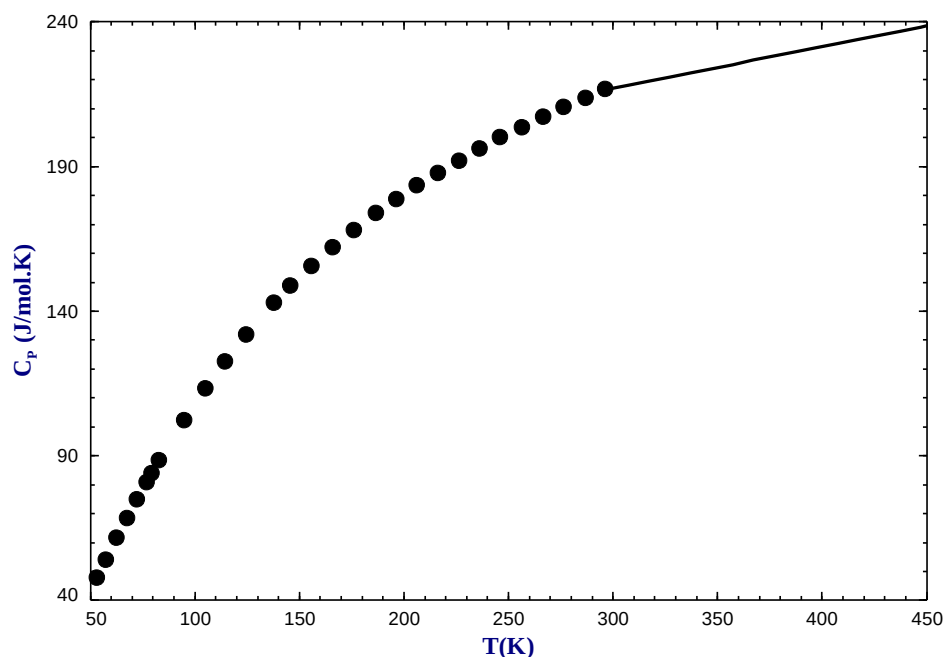


Figure 6.8 Calculated heat capacity at low temperatures for $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_1)$. Experimental data from [212] (●).

6.3.4 Potassium dimolybdate

6.3.4.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transition for $\text{K}_2\text{Mo}_2\text{O}_7$

Table 6.16 lists all data from the literature corresponding to the temperature and enthalpy change for the solid-solid transition of $\text{K}_2\text{Mo}_2\text{O}_7$. These data are very limited, and the enthalpy change was estimated as will be described later.

Table 6.16 Temperature and enthalpy change of solid-solid transition for $\text{K}_2\text{Mo}_2\text{O}_7$

$T_{\text{trans}} \text{ } S_1 \rightarrow S_2$ (°C)	$\Delta H_{\text{trans}} \text{ } S_1 \rightarrow S_2$ (kJ/mol)	Experimental Method	Reference
516.9-521.9	-	Calorimetry	[168]

519.4	2.190 (see text)	Weighted average of available data	This work

6.3.4.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for $K_2Mo_2O_7$

The properties of fusion (temperature and enthalpy change) collected from the literature are listed in Table 6.17. Owing to the lack of relevant data, the enthalpy of fusion was assessed as will be explained later.

Table 6.17 Temperature and enthalpy of fusion for $K_2Mo_2O_7$

$T_f \text{ } S_2 \rightarrow L \text{ } (^{\circ}C)$	$\Delta H_f \text{ } S_2 \rightarrow L \text{ } (kJ/mol)$	Experimental Method	Reference
484	-	Cooling curves with visual reading	[133]
491.9 ± 5	-	-	Reference 1 of [168]
541.9-556.9	-	Calorimetry	[168]
549.4	47.884 (see text)	Weighted average of available data	This work

6.3.4.3 Recommended thermodynamic data for potassium dimolybdate $K_2Mo_2O_7$

Our selected thermodynamic data ($\Delta H_{298.15 \text{ K}}^{\circ}$, $S_{298.15 \text{ K}}^{\circ}$, and C_p) for potassium dimolybdate $K_2Mo_2O_7$ are presented in Table 6.18.

Table 6.18 Selected thermodynamic properties of $K_2Mo_2O_7$

Compound	T Range (K)	$\Delta H_{298.15 \text{ K}}^{\circ}$ (J/mol)	$S_{298.15 \text{ K}}^{\circ}$ (J/mol.K)	C_p (J/mol.K)
$K_2Mo_2O_7 \text{ (s)}$	298.15 to 792.5 [168]	-2 293 222.0 [176]	290.5112 (This work)	$161.786912 + 0.162648816 T/K$

				+ 729689.6(T/K) ⁻² (This work)
K ₂ Mo ₂ O ₇ (S ₂)	298.15 to 822.5 [168]	-2 291 032.5 (This work)	293.2740 (This work)	Same as K ₂ Mo ₂ O ₇ (S ₁)
K ₂ Mo ₂ O ₇ (L)	298.15 to 822.5 822.5 to 1500 (This work) 1500 to 2000 (This work)	-2 243 148.0 (This work)	351.4922 (This work)	Same as K ₂ Mo ₂ O ₇ (S ₁) 165.301472 + 0.1594104 T/K (This work) 187.895072 + 0.144348 T/K (This work)

For the solid-solid transition temperature, only the data of Suponitskiy et al [168] obtained by calorimetry were available, and therefore our selected temperature is an average of the reported range of 790-795 K. For the sake of consistency, for the temperature of fusion, the data of the same authors were favored, and the average of the reported melting temperature range of 815-830 K was thus considered. The experimental values of [133, 168], which are much too low, were rejected.

To our knowledge, measurements of the enthalpy change for the solid-solid transition and fusion of K₂Mo₂O₇ are not available in the literature. By analogy with Na₂Mo₂O₇, as a first approximation, the entropy change for the solid-solid transition was assumed to be identical to that for K₂Cr₂O₇ (2.7628 J/mol.K). The transition temperature for K₂Mo₂O₇ has been evaluated as 792.5 K, which corresponds to an enthalpy change of about 2.190 kJ/mol. This is expected to be a reasonable estimate since both the low-temperature and high-temperature allotropes of K₂Mo₂O₇ and K₂Cr₂O₇ have the same crystal structure (with the same space group), the same alkali cation (K⁺) and very similar anionic radii (Mo₂O₇²⁻, Cr₂O₇²⁻). Similarly, the entropy of fusion of K₂Mo₂O₇ was assumed to be identical to that of K₂Cr₂O₇ (58.2182 J/mol.K). This permitted us to assess an enthalpy of fusion of about 47.884 kJ/mol from the previously evaluated temperature of fusion of 822.5 K.

To our knowledge, no experimental value of the standard enthalpy of formation at 298.15K ($\Delta H_{298.15\text{ K}}^\circ$) of K₂Mo₂O₇(S₁) has been reported in the literature. This quantity was assessed by us as -2,293,222 J/mol from the equation of Hisham and Benson [176] with an approach similar to that

described previously for $\text{Na}_2\text{Mo}_2\text{O}_7$. OQMD [128, 129] reported an enthalpy of formation at 0 K of -2,447,447 J/mol using DFT. The corresponding value given in Materials Project [130] is -2,276,571 J/mol.

The standard entropy at 298.15 K ($S_{298.15\text{ K}}^\circ$) of $\text{K}_2\text{Mo}_2\text{O}_7(\text{s}_1)$ was roughly estimated as 290.5112 J/mol.K from the exchange reaction $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_1) + \text{K}_2\text{MoO}_4(\text{s}_1) \rightarrow \text{K}_2\text{Mo}_2\text{O}_7(\text{s}_1) + \text{Na}_2\text{MoO}_4(\text{s}_1)$, assuming that $\Delta S = 0$ at 298.15K. The standard entropies at 298.15 K of $\text{Na}_2\text{MoO}_4(\text{s}_1)$ and $\text{K}_2\text{MoO}_4(\text{s}_1)$ were assessed by us previously [31], and that of $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_1)$ was estimated by us in this work.

Owing to the lack of relevant data, the heat capacities as a function of temperature for the various phases of $\text{K}_2\text{Mo}_2\text{O}_7$ were assessed from the exchange reactions $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_2) + \text{K}_2\text{MoO}_4(\text{s}_3) \rightarrow \text{K}_2\text{Mo}_2\text{O}_7(\text{s}) + \text{Na}_2\text{MoO}_4(\text{s}_4)$ (for the two allotropes) and $\text{Na}_2\text{Mo}_2\text{O}_7(\text{L}) + \text{K}_2\text{MoO}_4(\text{L}) \rightarrow \text{K}_2\text{Mo}_2\text{O}_7(\text{L}) + \text{Na}_2\text{MoO}_4(\text{L})$ (for the liquid phase), assuming that $\Delta C_p = 0$ at all temperatures.

6.3.5 Sodium ditungstate

6.3.5.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transition for $\text{Na}_2\text{W}_2\text{O}_7$

To our knowledge, no data are available in the literature for the properties of solid-solid transition of $\text{Na}_2\text{W}_2\text{O}_7$. As will be explained later, the temperature and enthalpy change were estimated very roughly as 677°C and 2.625 kJ/mol, respectively.

6.3.5.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for $\text{Na}_2\text{W}_2\text{O}_7$

The properties of fusion (temperature and enthalpy change) collected from the literature are listed in Table 6.19. The enthalpy of fusion has only been measured by Nolte and Kordes [146], using DTA.

Table 6.19 Temperature and enthalpy of fusion for $\text{Na}_2\text{W}_2\text{O}_7$

$T_f \text{ } S_2 \rightarrow L \text{ (}^\circ\text{C)}$	$\Delta H_f \text{ } S_2 \rightarrow L \text{ (kJ/mol)}$	Experimental Method	Reference
738	-	Differential thermographic (Kurnakov pyrometer) 10°C/min	[198]
730.9	95.353	DTA 1°C/min	[146]
730.9	-	Calorimetry	[181]
734.0	95.353	Weighted average of available data	This work

6.3.5.3 Recommended thermodynamic data for sodium ditungstate $\text{Na}_2\text{W}_2\text{O}_7$

Our selected thermodynamic data ($\Delta H_{298.15 \text{ K}}^\circ$, $S_{298.15 \text{ K}}^\circ$, and C_P) for sodium ditungstate $\text{Na}_2\text{W}_2\text{O}_7$ are presented in Table 6.20.

Table 6.20 Selected thermodynamic properties of $\text{Na}_2\text{W}_2\text{O}_7$

Compound	$T \text{ Range}$ (K)	$\Delta H_{298.15 \text{ K}}^\circ$ (J/mol)	$S_{298.15 \text{ K}}^\circ$ (J/mol.K)	C_P (J/mol.K)
$\text{Na}_2\text{W}_2\text{O}_7(\text{S}_1)$	298.15 to 950.2 This work	-2 485 296.0 [160]	254.3872 [212]	211.12 + 0.1072 T/K - 2566000 (T/K) ⁻² [181]
$\text{Na}_2\text{W}_2\text{O}_7(\text{S}_2)$	298.15 to 1007.1 This work	-2 482 670.9 This work	257.1450 This work	Same as $\text{Na}_2\text{W}_2\text{O}_7(\text{S}_1)$
$\text{Na}_2\text{W}_2\text{O}_7(\text{L})$	298.15 to 1007.1 1007.1 to 2000 This work	-2 387 317.5 This work	351.8310 This work	Same as $\text{Na}_2\text{W}_2\text{O}_7(\text{S}_1)$ 308.1768 This work

The experimental melting temperatures listed in Table 6.19 are in good agreement.

The temperature for the solid-solid transition of $\text{Na}_2\text{W}_2\text{O}_7$ is unknown and was finally assessed as about 950 K by assuming that the ratio $\left(\frac{T_f}{T_{\text{trans}}}\right)$ for $\text{Na}_2\text{W}_2\text{O}_7$ is identical to that for $\text{Na}_2\text{Mo}_2\text{O}_7$ (1.06). Strictly speaking, this assumption has no physical basis, but these two compounds have strong similarities. Indeed, both the low-temperature and high-temperature allotropes have the same crystal structure (with the same space group), the same alkali cation (Na^+), and very similar radii for the other cations ($\text{Mo}^{6+} = 0.59 \text{ \AA}$ and $\text{W}^{6+} = 0.60 \text{ \AA}$ in an octahedral geometry) [214] which are also in the same column of the periodic table.

Again, as a first approximation, the entropy change for the solid-solid transition of $\text{Na}_2\text{W}_2\text{O}_7$ was assumed to be identical to that for $\text{K}_2\text{Cr}_2\text{O}_7$ (2.7628 J/mol.K). This permitted us to assess an enthalpy change of about 2.625 kJ/mol from our estimated transition temperature of about 950 K for $\text{Na}_2\text{W}_2\text{O}_7$.

Using a cycle of calorimetric reactions, Koehler et al. [160] evaluated $\Delta H_{298.15 \text{ K}}^\circ = -2,485,296 \text{ J/mol}$ for $\text{Na}_2\text{W}_2\text{O}_7(\text{s}_1)$. This is to our knowledge the only experimental value available in the literature. Materials Project [130] reported an enthalpy of formation at 0 K of -2,345,558 J/mol using DFT, whereas OQMD [128, 129] reported a value of -2,563,133 J/mol (for the $\text{Cmc}2_1$ space group).

Weller and Kelley [212] reported a $S_{298.15 \text{ K}}^\circ$ value of $254.3872 \pm 2.092 \text{ J/mol.K}$ estimated by integration of their low-temperature heat capacity measurements obtained by calorimetry, with the use of the Einstein and Debye functions over the extrapolated temperature range of 0K to 51K.

Using calorimetry, Liu et al [181] performed heat content measurements ($H_T - H_{273.15\text{K}}$) for $\text{Na}_2\text{W}_2\text{O}_7$ from 273.15K to 979K. This permitted us to derive the heat capacity of both allotropes as a function of temperature (see Table 6.20), which was assumed to be valid up to our selected temperature of fusion of 1007.1 K.

Owing to the lack of data, the heat capacity of the liquid was estimated from the exchange reaction $\text{Na}_2\text{Mo}_2\text{O}_7(\text{L}) + 2 \text{Na}_2\text{WO}_4(\text{L}) \rightarrow 2 \text{Na}_2\text{MoO}_4(\text{L}) + \text{Na}_2\text{W}_2\text{O}_7(\text{L})$, assuming that $\Delta C_p = 0$ at all temperatures.

Calculated values of $H_T - H_{273.15\text{K}}$ are compared to the measurements of Liu et al [181] in Figure 6.9. The calculated heat capacity at low temperatures for $\text{Na}_2\text{W}_2\text{O}_7(\text{S}_1)$ is shown in Figure 6.10 along with the measurements of Weller and Kelley [212].

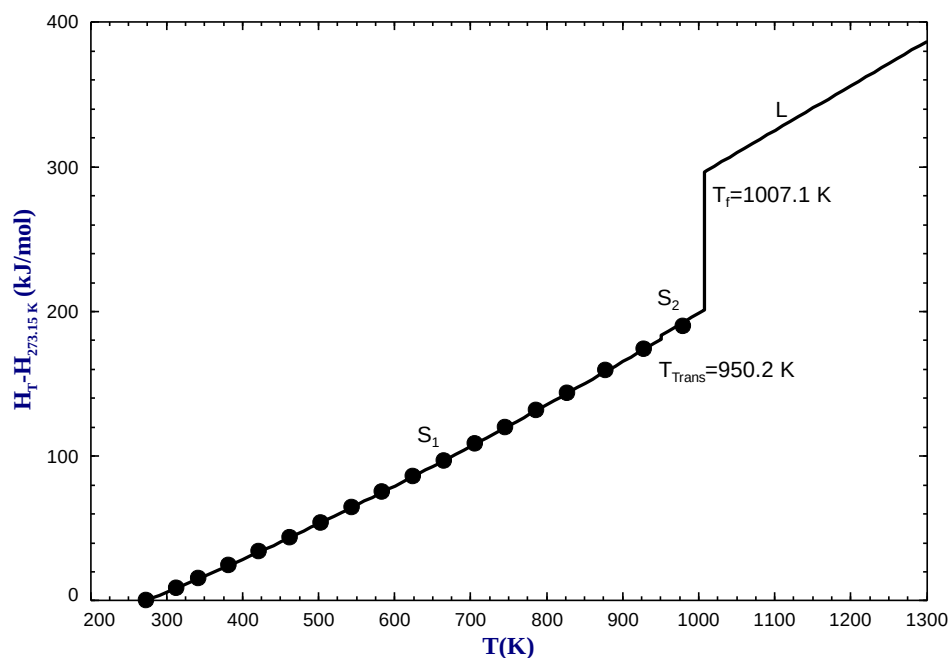


Figure 6.9 Calculated heat content $H_T - H_{273.15\text{K}}$ for $\text{Na}_2\text{W}_2\text{O}_7$. Experimental data from [181] (●).

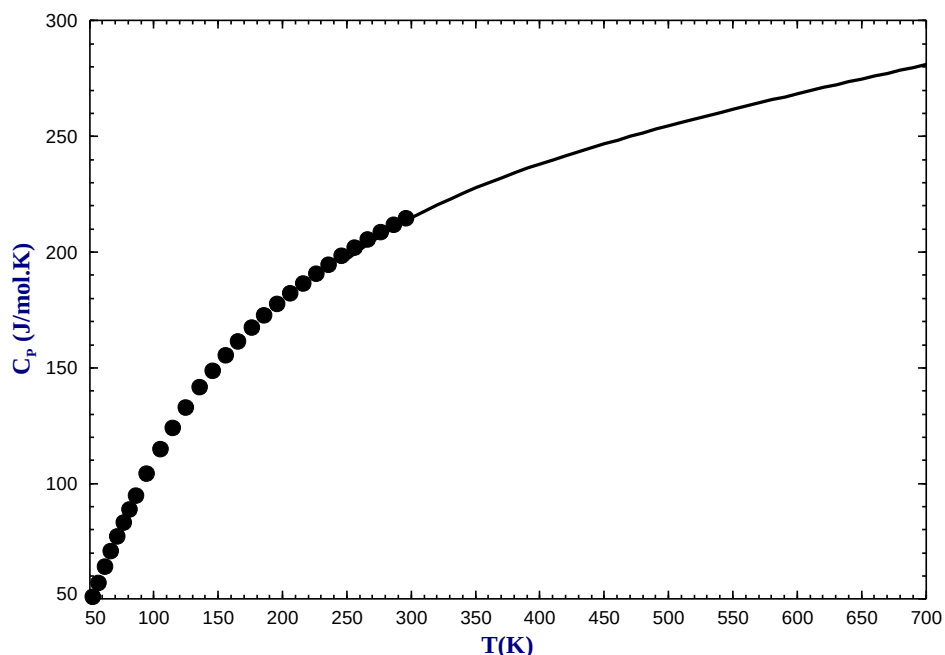


Figure 6.10 Calculated heat capacity at low temperatures for $\text{Na}_2\text{W}_2\text{O}_{7(\text{s1})}$. Experimental data from [212] (●).

6.3.6 Potassium ditungstate

6.3.6.1 Temperature (T_{trans}) and enthalpy change (ΔH_{trans}) of solid-solid transition for $\text{K}_2\text{W}_2\text{O}_7$

No data were found in the literature for the properties of solid-solid transition of $\text{K}_2\text{W}_2\text{O}_7$. As will be discussed later, the temperature and enthalpy change were assessed very roughly as 403°C and 1.868 kJ/mol, respectively.

6.3.6.2 Temperature (T_f) and enthalpy of fusion (ΔH_f) for $\text{K}_2\text{W}_2\text{O}_7$

Experimental properties of fusion for $\text{K}_2\text{W}_2\text{O}_7$ are presented in Table 6.21. The enthalpy of fusion was assessed by us as 49.665 kJ/mol, as will be explained later.

Table 6.21 Temperature and enthalpy of fusion for $K_2W_2O_7$

$T_f \text{ } S_2 \rightarrow L \text{ (}^\circ\text{C)}$	$\Delta H_f \text{ } S_2 \rightarrow L \text{ (kJ/mol)}$	Experimental Method	Reference
555	-	Cooling curves with visual reading	[133]
629.8	-	Drop calorimetry The corresponding value is the average of 604.5 and 655°C	[217]
580	49.665 (see text)	Weighted average of available data	This work

6.3.6.3 Recommended thermodynamic data for potassium ditungstate $K_2W_2O_7$

Our selected thermodynamic data ($\Delta H_{298.15 \text{ K}}^\circ$, $S_{298.15 \text{ K}}^\circ$, and C_p) for potassium ditungstate $K_2W_2O_7$ are presented in Table 6.22.

Table 6.22 Selected thermodynamic properties of $K_2W_2O_7$

Compound	T Range (K)	$\Delta H_{298.15 \text{ K}}^\circ$ (J/mol)	$S_{298.15 \text{ K}}^\circ$ (J/mol.K)	C_p (J/mol.K)
$K_2W_2O_7 (s_1)$	298.15 to 656.3 This work	-2 554 000 This work	242.8324	$207.97 + 0.10946 T/K - 1744000(T/K)^{-2}$
$K_2W_2O_7 (s_2)$	298.15 to 828.15 This work	-2 552 132.3 This work	245.5953 This work	Same as $K_2W_2O_7 (s_1)$
$K_2W_2O_7 (l)$	298.15 to 2000 This work	-2 502 467.3 This work	303.8240 This work	Same as $K_2W_2O_7 (s_1)$

The temperature for the solid-solid transition of $K_2W_2O_7$ has not been measured. It was finally estimated as about 676 K by assuming that the ratio $\left(\frac{T_f}{T_{\text{trans}}}\right)$ for $K_2W_2O_7$ is identical to that for $K_2Cr_2O_7$ (1.26). As mentioned previously, such an assumption has no physical basis but these two compounds have similarities. The high-temperature allotropes have the same crystal structure (with the same space group) and this is expected to apply to the low-temperature allotropes too. Also,

the two compounds have the same alkali cation (K^+) and very similar anionic radii ($W_2O_7^{2-}$, $Cr_2O_7^{2-}$).

Again, as a first approximation, the entropy change for the solid-solid transition of $K_2W_2O_7$ was assumed to be identical to that for $K_2Cr_2O_7$ (2.7628 J/mol.K). This permitted us to estimate an enthalpy change of about 1.868 kJ/mol from our assessed transition temperature of about 676 K for $K_2W_2O_7$. Similarly, the entropy of fusion of $K_2W_2O_7$ was assumed to be identical to that of $K_2Cr_2O_7$ (58.2222 J/mol.K). This corresponds to an enthalpy of fusion of about 49.665 kJ/mol based on our previously evaluated temperature of fusion of 853.1K.

The standard enthalpy at 298.15 K ($\Delta H_{298.15\text{ K}}^\circ$) of $K_2W_2O_7(s_1)$ was estimated as -2,554,000 J/mol by Kaganyuk and Trachevskii [218] using the effective charges on atoms in molecules and ions, calculated for the condition of equalization of potentials. To our knowledge, this is the only estimate available in the literature. Unfortunately, Hisham and Benson [176] have not considered alkali ditungstates in their work. Our selected $\Delta H_{298.15\text{ K}}^\circ$ value for $K_2Cr_2O_7(s_1)$ is about -82,170.4 J/mol more negative than that for $Na_2Cr_2O_7(s_1)$, and our selected $\Delta H_{298.15\text{ K}}^\circ$ value for $K_2Mo_2O_7(s_1)$ is about -49,241.7 J/mol more negative than that for $Na_2Mo_2O_7(s_1)$. Applying the corresponding average shift of -65,706.1 J/mol to our selected $\Delta H_{298.15\text{ K}}^\circ$ value for $Na_2W_2O_7(s_1)$ led to a very rough estimate of -2,551,002 J/mol for the standard enthalpy at 298.15 K of $K_2W_2O_7(s_1)$. The latter value compares very well to the estimate of Kaganyuk and Trachevskii [218], which was finally selected in the present work. This estimate may have limited accuracy since the same authors assessed a $\Delta H_{298.15\text{ K}}^\circ$ value of -2,329,000 J/mol for $Na_2Mo_2O_7(s_1)$, which is substantially more negative than our selected value of -2,243,980 J/mol based on experimental data from the literature. For $K_2W_2O_7$, OQMD [128, 129] reported an enthalpy of formation at 0 K of -2,605,586 J/mol using DFT. This value refers to the $P2_1/c$ space group, that is the high-temperature allotrope (S_2) according to our critical literature review (see Table 6.6). Materials Project [130] reported an enthalpy of formation at 0 K of -2,429,404 J/mol (for the $P2_1/c$ space group).

Owing to the lack of data, $S_{298.15\text{ K}}^\circ$ for $K_2W_2O_7(s_1)$ was roughly estimated as 242.8324 J/mol.K from the exchange reaction $K_2Cr_2O_7(s_1) + 2 K_2WO_4(s_1) \rightarrow 2 K_2CrO_4(s_1) + K_2W_2O_7(s_1)$,

assuming that $\Delta S = 0$ at 298.15 K. The standard entropies at 298.15 K of $\text{K}_2\text{WO}_4(\text{S}_1)$ and $\text{K}_2\text{CrO}_4(\text{S}_1)$ were assessed by us previously [31], and that of $\text{K}_2\text{Cr}_2\text{O}_7(\text{S}_1)$ was estimated by us in this work.

Using drop calorimetry, Chen et al [217] performed heat content measurements ($H_T - H_{273.15\text{K}}$) for $\text{K}_2\text{W}_2\text{O}_7$ from 273.15 K to 928.1 K. This permitted us to derive the heat capacity of both allotropes as a function of temperature (see Table 6.22), which was assumed to be valid up to our selected temperature of fusion of 853.1 K. Due to the lack of data, the same heat capacity expression was assumed to be valid for the pure liquid. Calculated values of $H_T - H_{273.15\text{K}}$ are shown along with the measurements of Chen et al [217] in Figure 6.11. As seen in this figure, the single measurement of these authors for the pure liquid is reasonably well reproduced.

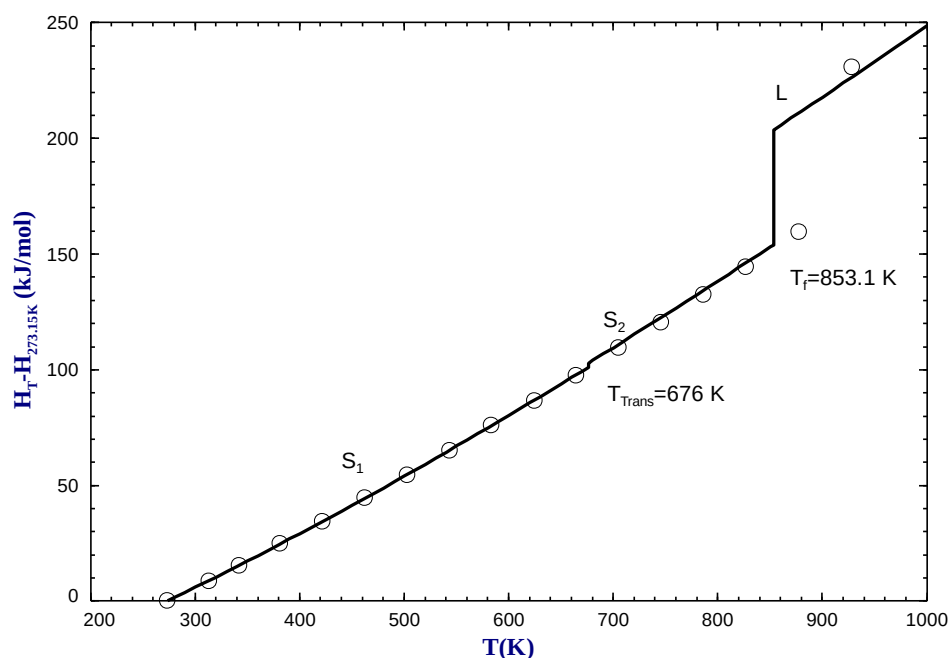


Figure 6.11 Calculated heat content $H_T - H_{273.15\text{K}}$ for $\text{K}_2\text{W}_2\text{O}_7$. Experimental data from [217] (○).

6.4 Discussion

Using our selected thermodynamic properties for the A_2MO_4 [31] and $\text{A}_2\text{M}_2\text{O}_7$ (present work) compounds (with A = Na or K, and M = Cr, Mo or W), the Gibbs energy changes were calculated as a function of temperature for all reactions of the type $2 \text{A}_2\text{MO}_4 = \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$. It permitted

us to conclude that these reactions are very limited in the temperature range of interest for the targeted industrial applications (that is, up to above the liquidus temperatures). The inversion temperatures at which the Gibbs energy changes become zero and then negative are always higher than about 3976°C (value for $\text{Na}_2\text{Mo}_2\text{O}_7$). At temperatures near or higher than these calculated inversion temperatures, the above reactions may be strongly shifted to the right with the formation of substantial oxide content in the liquid phase, and our thermodynamic model, which is being developed for the Na^+ , $\text{K}^+ // \text{Cl}^-$, SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$, O^{2-} system, will no longer be valid since only dilute amounts of oxides are considered in the liquid phase. Note that, at such high temperatures (which have very limited interest), the gas phase would need to be included in the calculations.

6.5 Conclusions

In this work, thermodynamic properties (standard enthalpy at 298.15 K, standard entropy at 298.15 K, and heat capacity as a function of temperature) were selected for all condensed phases of the compounds $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{W}_2\text{O}_7$ and $\text{K}_2\text{W}_2\text{O}_7$, based on a critical analysis of all available experimental data from the literature. Crystal structure data were also collected for all solid phases. Sometimes, some thermodynamic properties had to be estimated due to the lack of relevant data. A critical evaluation has been conducted previously for the thermodynamic properties of the compounds Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 and K_2WO_4 [31]. This permitted us to conclude that reactions of the type $2 \text{A}_2\text{MO}_4 = \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$ (where $\text{A} = \text{Na}, \text{K}$ and $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are very limited at least up to the temperature of fusion of A_2MO_4 . As mentioned previously, our selected heat capacities for $\text{Na}_2\text{Cr}_2\text{O}_7(\text{s}_1)$, $\text{Na}_2\text{Cr}_2\text{O}_7(\text{s}_2)$ and $\text{K}_2\text{Cr}_2\text{O}_7(\text{s}_2)$ are directly based on the heat content data of Nguyen-Duy and Dancy [202], which were very doubtful for both $\text{Na}_2\text{Cr}_2\text{O}_7(\text{L})$ and $\text{K}_2\text{Cr}_2\text{O}_7(\text{L})$. It is recommended to perform direct heat capacity measurements or heat content measurements for these three solid phases over relevant temperature ranges.

Evaluating the thermodynamic properties of the $\text{A}_2\text{M}_2\text{O}_7$ (present work) and A_2MO_4 [31] compounds is the first step towards the development of a thermodynamic model for the Na^+ , $\text{K}^+ // \text{Cl}^-$, SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$, WO_4^{2-} , $\text{W}_2\text{O}_7^{2-}$, O^{2-} system, which is relevant for high temperature corrosion of equipment such as heat-transfer tubes. This model combined with Gibbs energy minimization software will

permit us to perform phase equilibria calculations and investigate high temperature corrosion phenomena (typical temperature range of 600 to 950°C).

6.6 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. The authors would like to thank Dr. Paul Lafaye for fruitful discussions.

**CHAPITRE 7 ARTICLE 3 : 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**

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

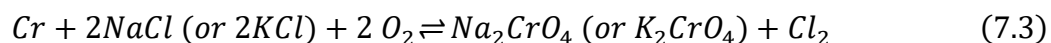
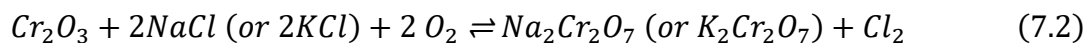
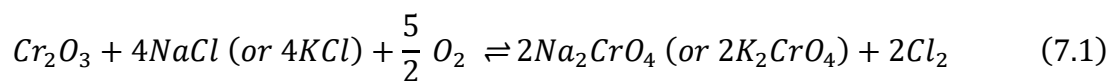
Submitted for publication in Chemical Engineering Science on July 5, 2023

Abstract: A complete critical evaluation of all available phase diagram and thermodynamic data has been performed for all condensed phases of the salt system (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂O) (diluted in free oxides), and optimized model parameters have been found. This system is important for the investigation of the chemistry of the different deposits formed in steel and stainless steel installations with Ni, Cr, Mo, W, and V as alloying elements during the combustion processes for energy production. The (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇) sub-system has been critically evaluated in previous articles. The Modified Quasichemical Model in the Quadruplet Approximation was used for both the molten salt phase and the high-temperature hexagonal solid solution (Na₂CO₃ + Na₂SO₄ + Na₂CrO₄ + K₂CO₃ + K₂SO₄ + K₂CrO₄) to take into account short-range-order between ions while the Compound Energy Formalism was used for all other solid solutions. Owing to the lack of data, DSC-TGA experiments were conducted for several compositions in a few common-ion binary sub-systems, with emphasis on solid-solid phase equilibria, and for one composition in a common-cation ternary sub-system. Also, the non-stoichiometric chrome-glaserite phase was investigated in particular at the composition (45 mol% Na₂CrO₄ + 55 mol% K₂CrO₄) using SEM-EDS and DSC-TGA, after annealing at 400°C for three weeks. The model parameters obtained for the binary and ternary sub-systems can be used to predict thermodynamic properties and phase equilibria for the multicomponent system.

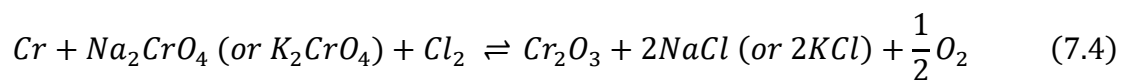
7.1 Introduction

Combustion-based energy production facilities are exposed to high-temperature gases containing impurities like SO_2 , Cl_2 , S_2 , and HCl , and corrosive products such as Na_2O , K_2O , NaOH , KOH , NaCl , and KCl [20, 26, 35]. These gases are a mixture of N_2 , CO_2 , CO , O_2 , and H_2O , and can contribute to corrosive deposit formation during ash evaporation in combustion. The most common deposits include KCl , NaCl , Na_2SO_4 , and K_2CO_3 [14, 26, 27, 35]. The presence of elements such as K, Na, Ca, Mg, Fe, Al, Si, P, S, Cl, C, H, and O during operation can also contribute to the formation of ashes and gases, that may cause different operational problems such as corrosion, slagging, fouling and agglomeration [24, 25]. The extent of corrosiveness depends on the composition of the gas and volatile ash, which in turn is influenced by factors such as the amount of air needed for combustion and the type of fuel used, along with any impurities that may be present [74]. Corrosion mechanisms are also associated with the nature of the steel or alloy used in combustion plants installation, as well as the formation of low melting point mixtures. Equipments made of steels and stainless steels with Ni, Cr, Mo, W, and V as alloying elements are particularly prone to this problem [19-21, 23]. The corrosion type experienced by the equipments under these conditions is known as hot corrosion. It takes place at elevated temperatures (from 600 to 950°C) [14, 57, 58] and is typically observed in municipal waste incineration, pyrolysis, and gasification of challenging fuels and feedstocks such as biomass waste. The temperature range over which corrosion typically occurs in certain combustion processes, such as black liquor combustion, is around 500°C. The threshold for such temperatures is determined by the lowest melting temperature of the ashes generated during the process.

According to Li et al [219], various complex reactions can lead to the formation of alkali chromates and alkali dichromates (including Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, and $\text{K}_2\text{Cr}_2\text{O}_7$), in which chromium has an oxidation state of 6+. Therefore, when an alkali salt deposit forms on the stainless steel surface, the protective Cr_2O_3 layer can be partially deteriorated according to the following reactions:



Both chromates and chlorine can interact as oxidants. Hence, the degradation kinetics of Cr-based alloys may be established from the following reaction [219]:



Typically, pure chromium is significantly more reactive than Cr_2O_3 with NaCl (or KCl) [219].

Lindberg et al [39-41] developed previously an accurate thermodynamic model for the Na^+ , K^+ // Cl^- , CO_3^{2-} , SO_4^{2-} , $S_2O_7^{2-}$ reciprocal system. The present paper focuses on adding alkali chromates (Na_2CrO_4 , K_2CrO_4) and alkali dichromates ($Na_2Cr_2O_7$, $K_2Cr_2O_7$) to this existing model. As a first step, an assessment of the thermodynamic properties (standard enthalpy of formation $\Delta H_{298.15 K}^\circ$ from the elements in their stable standard state at 298.15K and 1 atm, absolute (third law) entropy $S_{298.15 K}^\circ$ referenced at 298.15K and 1 atm, and heat capacity C_P as a function of temperature) of Na_2CrO_4 , K_2CrO_4 , $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ was conducted by us using the available data from the literature and also newly obtained differential scanning calorimetry (DSC) measurements (for Na_2CrO_4 and K_2CrO_4) [31, 34]. In addition, in those studies, extensive information on the crystal structures of all allotropes of the four compounds was collected in order to identify possible solid solutions forming with other considered salts.

The present paper describes a thermodynamic model for the ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7 + Na_2O + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7 + K_2CrO_4 + K_2Cr_2O_7 + K_2O$) system. The optimization of the ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7$) sub-system has been presented in previous articles [39-41]. The free oxides (Na_2O and K_2O) are present in dilute amounts in the liquid solution since reactions of the type $2 A_2CrO_4 = A_2Cr_2O_7 + A_2O$ (where $A = Na, K$) are very limited up to above the liquidus temperatures [34]. In this work, owing to the lack of data, differential scanning calorimetry (DSC)-thermogravimetric analysis (TGA) experiments were performed for several compositions in a few common-ion binary sub-systems (($Na_2CO_3 + Na_2CrO_4$), ($K_2CO_3 + K_2CrO_4$), and ($Na_2CrO_4 + K_2CrO_4$)), with emphasis on solid-solid phase equilibria. In addition, the chrome-glaserite solid solution was investigated in particular at the composition (45 mol% $Na_2CrO_4 + 55$ mol% K_2CrO_4) after annealing, using both scanning electron microscopy (SEM)-energy dispersive spectroscopy (EDS) and DSC-TGA. Finally, the common-cation ternary mixture (55.0 mol% $KCl + 28.0$ mol% $K_2CO_3 + 17.0$ mol%

K₂CrO₄) (corresponding to the predicted ternary eutectic) was studied by DSC-TGA.

All calculations and optimizations were performed using the FactSage software package [42].

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

This study used directly the thermodynamic data ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_P) previously selected for the condensed pure compounds of the (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂O) system [31, 34, 39, 40, 220]. Chartrand and Pelton [220] evaluated the thermodynamic data for NaCl and KCl, based on the compilation of Barin et al [127]. Lindberg et al [39, 40] assessed the thermodynamic properties of Na₂CO₃, Na₂SO₄, K₂CO₃, K₂SO₄, Na₂S₂O₇ and K₂S₂O₇ based on the NIST-JANAF thermodynamic data compilation [170] and the work of Dessureault et al [221].

The thermodynamic data for Na₂CrO₄, K₂CrO₄, Na₂Cr₂O₇ and K₂Cr₂O₇ were directly taken from our previous studies [31, 34] and were based on experimental data available in the literature, and our XRD analysis and DSC-TGA measurements (for Na₂CrO₄ and K₂CrO₄). Finally, the thermodynamic properties of Na₂O and K₂O were taken directly from the FToxid database in FactSage [42].

Table 7.1 provides a summary of the crystal structures and space groups of all relevant pure salt compounds. For the allotropes of Na₂CrO₄, K₂CrO₄, Na₂Cr₂O₇ and K₂Cr₂O₇, the most probable crystal structures and space groups were discussed by us previously [31, 34].

Table 7.1 Crystal structures and space groups of all relevant pure salt compounds

Pure compound	Allotrope	Crystal structure	Space group	Pearson Symbol / Phase Prototype	Reference
NaCl	NaCl	Cubic	Fm $\bar{3}$ m (225)	cF8 / NaCl	FactSage (FTsalt database) [42]
KCl	KCl	Cubic	Fm $\bar{3}$ m (225)	cF8 / NaCl	FactSage (FTsalt database) [42]

Na ₂ CO ₃	Na ₂ CO ₃ (S ₁)	Monoclinic	C2/m (12)	mS24 / γ -Na ₂ CO ₃ -a	database) [42, 222]
	Na ₂ CO ₃ (S ₂)	Monoclinic	C2/m (12)	mS24 / β -Na ₂ CO ₃ -b	
	Na ₂ CO ₃ (S ₃)	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	
K ₂ CO ₃	K ₂ CO ₃ (S ₁)	Monoclinic	P2 ₁ /c (14)	mP24 / K ₂ CO ₃	FactSage (FTsalt database) [42] [40]
	K ₂ CO ₃ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	
Na ₂ SO ₄	Na ₂ SO ₄ (S ₃)	Orthorhombic	Fddd (70)	oF56 / Na ₂ SO ₄	FactSage (FTsalt database) [42], [39]
	Na ₂ SO ₄ (S ₁)	Orthorhombic	Cmcm (63)	oS28 / Na ₂ CrO ₄	
	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	P $\bar{1}$ (2)	aP22 / Cd ₂ P ₂ O ₇	FactSage (FTsalt database) [42], [223, 224]
K ₂ SO ₄	K ₂ SO ₄ (S ₁)	Orthorhombic	Pnma (62)	oP28 / K ₂ SO ₄	FactSage (FTsalt database) [42], [39]
	K ₂ SO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	
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 database) [42], [223]
	K ₂ S ₂ O ₇ (S ₂)	-	-	-	
Na ₂ CrO ₄	Na ₂ CrO ₄ (S ₁)	Orthorhombic	Cmcm (63)	oS28 / Na ₂ CrO ₄	[31, 225]
	Na ₂ CrO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	*	
Na ₂ Cr ₂ O ₇	Na ₂ Cr ₂ O ₇ (S ₁)	Triclinic	P $\bar{1}$ (2)	aP44 / Na ₂ Cr ₂ O ₇	[34, 226, 227]
	Na ₂ Cr ₂ O ₇ (S ₂)	Triclinic	A $\bar{1}$ (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	[31, 228]
	K ₂ CrO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	*	
K ₂ Cr ₂ O ₇	K ₂ Cr ₂ O ₇ (S ₁)	Triclinic	P $\bar{1}$ (2)	aP44 / K ₂ Cr ₂ O ₇	[34, 223, 229]
	K ₂ Cr ₂ O ₇ (S ₂)	Monoclinic	P2 ₁ /c (14)	-	

* The corresponding Pearson symbols / prototypes for Na₂CrO₄(S₂) and K₂CrO₄(S₂) were not available to our

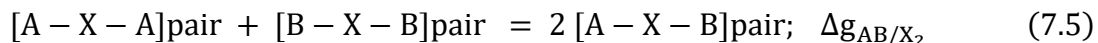
knowledge. Thus, since these two compounds have the same crystal structure and space group as $\text{Na}_2\text{CO}_3(\text{S}_3)$, $\text{Na}_2\text{SO}_4(\text{S}_2)$, $\text{K}_2\text{CO}_3(\text{S}_2)$, and $\text{K}_2\text{SO}_4(\text{S}_2)$, they were assumed to have the same Pearson symbol / prototype phase (that is, hP22 / K_2SO_4).

7.3 Thermodynamic model for the liquid phase

The liquid solution for the ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{O}$) system (diluted in free oxides) was modeled using the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA) [45]. The cations (Na^+ and K^+ in the present case) and the anions (Cl^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and O^{2-} in the present case) are distributed over a cationic and an anionic sublattice, respectively. The MQMQA evaluates coupled 1st- and 2nd-nearest-neighbour short-range order within a sublattice and between sublattices. A quadruplet such as $\text{Na}_2(\text{CrO}_4)_2$, $\text{NaK}(\text{CrO}_4)_2$, $\text{Na}_2(\text{Cl})(\text{CrO}_4)$ or $\text{NaK}(\text{Cl})(\text{CrO}_4)$ consists of two 2nd-nearest-neighbour cations and two 2nd-nearest-neighbour anions, which are mutual 1st-nearest-neighbours. Each quadruplet has a Gibbs energy. Quadruplets mix randomly, constrained by an elemental mass balance. The equilibrium quadruplet composition (configuration) is the one that minimizes the Gibbs energy of the melt at a given temperature, pressure and composition, and thus results in an equilibrium configuration that reflects 1st- and 2nd-nearest-neighbour short-range order.

The model is described in detail in reference [45]. Although the degree of short-range ordering is not large in the system studied in the present work, we have shown that the Modified Quasichemical Model (MQM) clearly provides a better representation than a random mixing model, especially in reciprocal ternary sub-systems. For example, in reference [230], the MQM and the Bragg-Williams random mixing model are both applied to some binary and ternary metallic liquid solutions exhibiting short-range ordering, and the main weaknesses of the random mixing model are shown. In a liquid metal, the various atoms are assumed to distribute on the sites of a quasi-lattice, and 1st-nearest-neighbour interactions then have to be taken into account. The conclusions from the reference [230] directly apply to multicomponent common-ion molten salt systems, in which only 2nd-nearest-neighbour (either cation-cation or anion-anion) interactions have to be considered. The system considered in this work is a reciprocal molten salt solution (i.e. a solution with more than one cation and more than one anion). In such liquid solutions, large

deviations from ideal mixing may occur due to the strong 1st-nearest-neighbour (cation-anion) interactions. Modeling such solutions is a challenge. If, simultaneously, there is also strong 2nd-nearest-neighbour (cation-cation) short-range ordering, the solution becomes even more difficult to model. Second-nearest-neighbour (cation-cation) short-range ordering is described in terms of the following equilibrium:



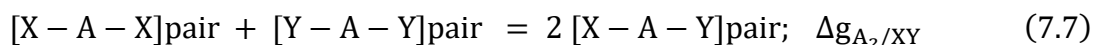
where A and B are two different cations (Na^+ and K^+ in the present case), and X is an anion. As the Gibbs energy change $\Delta g_{AB/X_2}$ becomes progressively more negative, reaction (7.5) is shifted to the right, [A-X-B] pairs predominate and 2nd-nearest-neighbour (cation-cation) short-range ordering results. $\Delta g_{AB/X_2}$ is a model parameter that can be expressed as a function of composition by an empirical polynomial expression (equation [11] in reference [78]).

When reciprocal salt solutions are formed, first-nearest-neighbour (cation-anion) short-range ordering can occur. Its extent is related to the Gibbs energy change for the following exchange reaction:



where A and B are two different cations (Na^+ and K^+ in the present case), and X and Y are two different anions. If $\Delta g_{AB/XY}^{\text{exchange}}$ is negative, then [A-Y] and [B-X] 1st-nearest-neighbour pairs predominate. For example, $\Delta g_{\text{NaK/Cl}(\text{CrO}_4)}^{\text{exchange}}$ for the exchange reaction $\text{KCl(l)} + 0.5 \text{Na}_2\text{CrO}_4(\text{l}) \leftrightarrow \text{NaCl(l)} + 0.5 \text{K}_2\text{CrO}_4(\text{l})$ is calculated to be about -4.2 kJ/mol at 1250K (i.e. above the highest melting temperature of the four pure salts).

In the MQMQA, the parameters are the Gibbs energies of the quadruplet-formation reactions, similar to reaction (7.5). It has to be noted that, to a lesser extent, 2nd-nearest-neighbour anion-anion ordering can play a role. Therefore, the following pair exchange reactions are also considered:



where A is a cation (Na^+ or K^+ in the present case), and X and Y are two different anions.

To obtain quantitative fits, small empirical “ternary reciprocal parameters” may have to be included. As described previously [45], these parameters represent the Gibbs energies of formation of the ABXY quadruplets from the binary quadruplets according to:

$$\frac{1}{2}(\text{ABX}_2 + \text{ABY}_2 + \text{A}_2\text{XY} + \text{B}_2\text{XY}) = 2 (\text{ABXY}); \quad \Delta g_{\text{AB/XY}} \quad (7.8)$$

where $\Delta g_{\text{AB/XY}}$ is expanded as an empirical polynomial in the mole fractions $x_{\text{A}_2/\text{X}_2}$, $x_{\text{A}_2/\text{Y}_2}$, $x_{\text{B}_2/\text{X}_2}$ and $x_{\text{B}_2/\text{Y}_2}$ of the A_2X_2 , A_2Y_2 , B_2X_2 and B_2Y_2 unary quadruplets as follows:

$$\Delta g_{\text{AB/XY}} = \Delta g_{\text{AB/XY}}^0 + \sum_{i \geq 1} \left[g_{\text{AB/XY}(\text{AX})}^i x_{\text{A}_2/\text{X}_2}^i + g_{\text{AB/XY}(\text{BX})}^i x_{\text{B}_2/\text{X}_2}^i + g_{\text{AB/XY}(\text{AY})}^i x_{\text{A}_2/\text{Y}_2}^i + g_{\text{AB/XY}(\text{BY})}^i x_{\text{B}_2/\text{Y}_2}^i \right] \quad (7.9)$$

The empirical parameters $\Delta g_{\text{AB/XY}}^0$ and $g_{\text{AB/XY}(\text{AX})}^i$, etc. may be temperature-dependent and are obtained from the optimization of thermodynamic and phase diagram data in the ternary reciprocal system A, B // X, Y. They should all be relatively small.

In a previous publication [45], “default values” of the 2nd-nearest-neighbour (cation-cation or anion-anion) “coordination numbers” for the ABXY quadruplets were proposed (equation [23] of reference [45]). These “default values” were used for the Na, K // SO_4 , CrO_4 , Na, K // CO_3 , CrO_4 and Na, K // Cl, CrO_4 ternary reciprocal systems modelled in this work. Note that the 2nd-nearest-neighbour “coordination numbers” are model parameters. In particular, the compositions of maximum short-range ordering in the A, B // X and A // X, Y common-ion binary systems are determined by the ratios $(Z_{\text{AB/X}_2}^{\text{B}}/Z_{\text{AB/X}_2}^{\text{A}})$ and $(Z_{\text{A}_2/\text{XY}}^{\text{Y}}/Z_{\text{A}_2/\text{XY}}^{\text{X}})$ [77, 78], respectively, where $Z_{\text{AB/X}_2}^i$ and $Z_{\text{A}_2/\text{XY}}^i$ are the 2nd-nearest-neighbour “coordination numbers” of the ion i when all i exist in ABX_2 and A_2XY quadruplets, respectively. Reasonable absolute values of the 2nd-nearest-neighbour “coordination numbers” are chosen in order to best reproduce the available phase diagram and thermodynamic data, and the selected absolute values may differ from the real (experimental) values.

As discussed in reference [78], it is necessary to designate all ternary common-cation sub-systems of the $(\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7)$ main system as either “symmetric” or “asymmetric”. The liquid model consists of the Na^+ and K^+ cations, and of the following main anions: Cl^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$. All anions are separated into two different chemical groups, according to their valence: group 1 = Cl^- ; group 2 = CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$. For all ternary common-cation sub-systems containing NaCl or KCl (such as $(\text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ considered in the present work), 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 $(\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4)$ considered in this work), all three anions belong to the same group; a Kohler-like (symmetric) interpolation method is then used. The parameters $\Delta g_{\text{AB}/\text{X}_2}$ (reaction (7.5)) and $\Delta g_{\text{A}_2/\text{XY}}$ (reaction (7.7)) are expanded, through optimization with available experimental data for the A, B // X and A // X, Y common-ion binary systems, respectively, as empirical polynomials in χ_{ij} and χ_{ji} . Once an interpolation method has been chosen for each ternary common-ion sub-system, the composition variables χ_{ij} and χ_{ji} are defined unambiguously [78]. For ternary common-cation sub-systems of the type $(\text{AX} + \text{AY} + \text{AZ})$ (where A is Na^+ or K^+ , and X, Y, Z are three different anions), terms may be added that give the effect of the third component, AZ, on the quadruplet-formation energy of the binary A_2XY quadruplet, $\Delta g_{\text{A}_2/\text{XY}}$. This is done by introducing the empirical ternary parameter $g_{\text{A}/\text{XY}(\text{Z})}^{\text{ijk}}$, which can be obtained through the optimization of thermodynamic and phase diagram data in the common-cation ternary system A // X, Y, Z.

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

$$G = \sum n_{ij/\text{kl}} g_{ij/\text{kl}} - T \Delta S^{\text{config}} \quad (7.10)$$

where $n_{ij/\text{kl}}$ refers to the number of moles of the various quadruplets (unary, binary, and reciprocal), $g_{ij/\text{kl}}$ is the Gibbs energy of the quadruplets, and ΔS^{config} is the configurational entropy of mixing which includes the quasichemical short-range ordering terms. The latter is calculated from a random distribution of all quadruplets over “quadruplet positions”. However, there is no exact mathematical expression for this distribution, and an approximate expression for ΔS^{config} was originally given in reference [45].

As reported previously [231], the MQMQA has been improved. 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 , defined in equation [17] of reference [45] and related to the ratio between the 2nd-nearest-neighbour and 1st-nearest-neighbour “coordination numbers” for a species i , is no longer constant. These recent improvements have been made in order to address the limitation of the previous model (see paragraph 3.3.4 in reference [232]), when the Gibbs energy change $\Delta g_{AB/XY}^{\text{exchange}}$ of reaction (7.6) becomes very negative. The parameter ζ has been defined previously [45] as:

$$\zeta = 2(Z/z) \quad (7.11)$$

where z and Z are the 1st-nearest-neighbour (cation-anion) and 2nd-nearest-neighbour (cation-cation or anion-anion) “coordination numbers”, respectively. ζ has previously [233] been set to 2.4 for the Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} // F^- , Cl^- reciprocal system. It has been shown [45] that ζ is equal to the number of quadruplets emanating from, or containing, a 1st-nearest-neighbour [A-X] pair. In the improved version of the MQMQA, the notation $\zeta_{A/X}$ is used and this parameter is

defined as:

$$\zeta_{A/X} = 2Z_{A_2/X_2}^A Z_{A_2/X_2}^X / (Z_{A_2/X_2}^A + Z_{A_2/X_2}^X) \quad (7.12)$$

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 A_2X_2 quadruplets. The values of the 2nd-nearest-neighbour “coordination numbers” and of the newly optimized model parameters for the liquid phase of the Na^+ , K^+ // Cl^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, O^{2-} reciprocal system (diluted in free oxides) are given in Tables 7.2 and 7.3, respectively.

Finally, the values of $\zeta_{A/X}$ (equation (7.12)) for the Na^+ , K^+ // Cl^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, O^{2-} reciprocal system are :

$$\zeta_{A/X} = 4; \quad \zeta_{A/Cl} = 6 \quad (7.13)$$

where $A = \text{Na}^+$, K^+ ; and $X = \text{CO}_3^{2-}$, SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, O^{2-} .

Table 7.2 2nd-nearest-neighbour “coordination numbers” for the quadruplets ABXY of the newly optimized systems of the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, O²⁻ liquid phase

A	B	X	Y	$Z_{AB/XY}^A$	$Z_{AB/XY}^B$	$Z_{AB/XY}^X$	$Z_{AB/XY}^Y$
Na	Na	Cl	Cl	6	6	6	6
K	K	Cl	Cl	6	6	6	6
Na	Na	CO ₃	CO ₃	3	3	6	6
K	K	CO ₃	CO ₃	3	3	6	6
Na	Na	SO ₄	SO ₄	3	3	6	6
K	K	SO ₄	SO ₄	3	3	6	6
Na	Na	S ₂ O ₇	S ₂ O ₇	3	3	6	6
K	K	S ₂ O ₇	S ₂ O ₇	3	3	6	6
Na	Na	CrO ₄	CrO ₄	3	3	6	6
K	K	CrO ₄	CrO ₄	3	3	6	6
Na	Na	Cr ₂ O ₇	Cr ₂ O ₇	3	3	6	6
K	K	Cr ₂ O ₇	Cr ₂ O ₇	3	3	6	6
Na	Na	O	O	3	3	6	6
K	K	O	O	3	3	6	6
Na	Na	Cl	CrO ₄	4	4	4	8
K	K	Cl	CrO ₄	4	4	4	8
Na	Na	CO ₃	CrO ₄	3	3	6	6
Na	Na	SO ₄	CrO ₄	3	3	6	6

K	K	CO ₃	CrO ₄	3	3	6	6
K	K	SO ₄	CrO ₄	3	3	6	6
Na	K	CrO ₄	CrO ₄	3	3	6	6
K	K	Cl	Cr ₂ O ₇	4	4	6	6
K	K	CrO ₄	Cr ₂ O ₇	3	3	6	6
Na	Na	CrO ₄	Cr ₂ O ₇	3	3	6	6
Na	K	Cr ₂ O ₇	Cr ₂ O ₇	3	3	6	6

The 2nd-nearest-neighbour "coordination numbers" for the ABXY quadruplets of the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻ liquid were given previously in the work of Lindberg et al [39-41], and they were used directly in the present work.

Table 7.3 Model parameters optimized in the present work for the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, O²⁻ liquid phase (diluted in free oxides)

System	Model parameter (J/mol)
(NaCl + Na ₂ CrO ₄)	$\Delta g_{\text{Na}_2/(\text{Cl})(\text{CrO}_4)} = -250.0 - 750.0 \chi_{(\text{CrO}_4)(\text{Cl})}$
(Na ₂ CO ₃ + Na ₂ CrO ₄)	$\Delta g_{\text{Na}_2/(\text{CO}_3)(\text{CrO}_4)} = 400.0 + 1,000.0 \chi_{(\text{CrO}_4)(\text{CO}_3)}$
(K ₂ CO ₃ + K ₂ CrO ₄)	$\Delta g_{\text{K}_2/(\text{CO}_3)(\text{CrO}_4)} = 1,000.0$
(Na ₂ CrO ₄ + K ₂ CrO ₄)	$\Delta g_{\text{NaK}/(\text{CrO}_4)_2} = -1,419.6$
(KCl + K ₂ Cr ₂ O ₇)	$\Delta g_{\text{K}_2/(\text{Cl})(\text{Cr}_2\text{O}_7)} = -1,400.0$
(K ₂ CO ₃ + K ₂ SO ₄ + K ₂ CrO ₄)	$g_{\text{K}/(\text{CrO}_4)(\text{CO}_3)[\text{SO}_4]}^{101} = -9,000.0$

$(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4)$	$\Delta g_{\text{NaK}/(\text{CO}_3)(\text{CrO}_4)} = -900.0 - 9,500.0x_{\text{Na}_2/(\text{CO}_3)_2} - 9,000.0x_{\text{K}_2/(\text{CrO}_4)_2}$

7.4 Thermodynamic model for the solid solutions

In this work, various solid solutions were modeled in the Na^+ , $\text{K}^+ // \text{Cl}^-$, CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ main system. These are described in detail in Table 7.4, and all optimized model parameters are given. The Na^+ , $\text{K}^+ // \text{CO}_3^{2-}$, SO_4^{2-} , CrO_4^{2-} sub-system exhibits a hexagonal solid solution (hP22) at high temperatures, with complete mutual miscibility over the entire composition range.

This reciprocal solid solution was modeled using the MQMQA [45] with two sublattices, where the cations reside on the cationic sublattice and the anions reside on the anionic sublattice. Lindberg et al [39] previously modeled the high-temperature ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$) hexagonal solid solution using the Compound Energy Formalism (CEF) [46-48], in which the Na^+ and K^+ cations were randomly distributed on the cationic sublattice. Approximately at the same time, Coursol et al [234] modeled the high-temperature ($\text{Na}_2\text{SO}_4 + \text{CaSO}_4$) solid solution (with CaSO_4 in limited amounts) using the MQM in the pair approximation, which takes account of 2nd-nearest-neighbour (cation-cation) short-range-order. This solid solution displays a maximum evidenced by the available experimental data and well reproduced by the MQM. The MQM is more suited than the CEF to model complex solid solutions such as ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$) dissolving divalent cation sulfates (such as CaSO_4 , ZnSO_4 and PbSO_4). In a recent work [235], the MQM was retained, thus permitting us to add ZnSO_4 and PbSO_4 as solutes in the high-temperature ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$) hexagonal solid solution. For the sake of consistency, the MQMQA was used in the present work to model the hP22 solid solution (with Na^+ and K^+ as the cations, and CO_3^{2-} , SO_4^{2-} and CrO_4^{2-} as the anions). In addition, several low-temperature solid solutions displaying limited solubility were considered. The CEF was used to model those.

Three sublattices were required for the chrome-glaserite phase $K_3Na(CrO_4)_2$, which exhibits significant non-stoichiometry at temperatures above room temperature [84, 90]. In all other cases, only two sublattices were necessary. For instance, let us consider the oF56 solid solution which consists of the orthorhombic low-temperature allotrope $Na_2SO_{4(S3)}$ dissolving Na_2CrO_4 , K_2SO_4 and K_2CrO_4 . The sublattice structure $(Na^+, K^+)_2(SO_4^{2-}, CrO_4^{2-})$ is used, where Na^+ and K^+ reside on the cationic sublattice C while SO_4^{2-} and CrO_4^{2-} reside on the anionic sublattice A. The molar Gibbs energy of the solution is given by the following expression :

$$G_m = y_{Na^+}^C y_{SO_4^{2-}}^A G_{Na^+:SO_4^{2-}}^\circ + y_{Na^+}^C y_{CrO_4^{2-}}^A G_{Na^+:CrO_4^{2-}}^\circ + y_{K^+}^C y_{SO_4^{2-}}^A G_{K^+:SO_4^{2-}}^\circ + \\ + y_{K^+}^C y_{CrO_4^{2-}}^A G_{K^+:CrO_4^{2-}}^\circ + 2RT(y_{Na^+}^C \ln y_{Na^+}^C + y_{K^+}^C \ln y_{K^+}^C) + RT(y_{SO_4^{2-}}^A \ln y_{SO_4^{2-}}^A + \\ y_{CrO_4^{2-}}^A \ln y_{CrO_4^{2-}}^A) + G^E \quad (7.14)$$

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 $y_{SO_4^{2-}}^A$ and $y_{CrO_4^{2-}}^A$ are the site fractions of SO_4^{2-} and CrO_4^{2-} on the anionic sublattice A. The standard molar Gibbs energies of the end-member components Na_2SO_4 , K_2SO_4 , Na_2CrO_4 and K_2CrO_4 are represented by $G_{Na^+:SO_4^{2-}}^\circ$, $G_{K^+:SO_4^{2-}}^\circ$, $G_{Na^+:CrO_4^{2-}}^\circ$, and $G_{K^+:CrO_4^{2-}}^\circ$, respectively. The fifth and sixth terms in equation (7.14) account for the ideal entropy of mixing, assuming a random distribution of the cations on the cationic sublattice and of the anions on the anionic sublattice (Temkin type, [236]). The final term refers to the molar excess Gibbs energy and has the following general expression:

$$G^E = y_{Na^+}^C y_{K^+}^C y_{SO_4^{2-}}^A L_{Na^+,K^+:SO_4^{2-}} + y_{Na^+}^C y_{K^+}^C y_{CrO_4^{2-}}^A L_{Na^+,K^+:CrO_4^{2-}} \\ + y_{Na^+}^C y_{SO_4^{2-}}^A y_{CrO_4^{2-}}^A L_{Na^+:SO_4^{2-},CrO_4^{2-}} + y_{K^+}^C y_{SO_4^{2-}}^A y_{CrO_4^{2-}}^A L_{K^+:SO_4^{2-},CrO_4^{2-}} \\ + y_{Na^+}^C y_{K^+}^C y_{SO_4^{2-}}^A y_{CrO_4^{2-}}^A L_{Na^+,K^+:SO_4^{2-},CrO_4^{2-}} \quad (7.15)$$

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 $L_{i \geq 0}^i (y_A - y_B)^i$ as a function of site fractions are usually used. Note that no excess Gibbs energy term was required in the present work to model the oF56 solid solution.

Table 7.4 Description and list of optimized model parameters for the various solid solutions in the Na^+ , K^+ // Cl^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ main system modeled in the present work

Hexagonal solid solution hP22

High-temperature allotropes $\text{Na}_2\text{CO}_3(\text{S3})$, $\text{K}_2\text{CO}_3(\text{S2})$, $\text{Na}_2\text{SO}_4(\text{S2})$, $\text{K}_2\text{SO}_4(\text{S2})$, $\text{Na}_2\text{CrO}_4(\text{S2})$ and $\text{K}_2\text{CrO}_4(\text{S2})$ with mutual solubility

$\text{P6}_3/\text{mmc}$ space group

Sublattice structure: $(\text{Na}^+, \text{K}^+)_2(\text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{CrO}_4^{2-})$

Use of the MQMQA

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

$$g_{\text{Na}_2\text{CO}_3}^\circ = g_{\text{Na}_2\text{CO}_3(\text{S3})}^\circ$$

$$g_{\text{K}_2\text{CO}_3}^\circ = g_{\text{K}_2\text{CO}_3(\text{S2})}^\circ$$

$$g_{\text{Na}_2\text{SO}_4}^\circ = g_{\text{Na}_2\text{SO}_4(\text{S2})}^\circ$$

$$g_{\text{K}_2\text{SO}_4}^\circ = g_{\text{K}_2\text{SO}_4(\text{S2})}^\circ$$

$$g_{\text{Na}_2\text{CrO}_4}^\circ = g_{\text{Na}_2\text{CrO}_4(\text{S2})}^\circ$$

$$g_{\text{K}_2\text{CrO}_4}^\circ = g_{\text{K}_2\text{CrO}_4(\text{S2})}^\circ$$

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 $A = \text{Na}^+$, K^+ and $X = \text{CO}_3^{2-}$, SO_4^{2-} , CrO_4^{2-}).

The following interaction parameters for $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4)$, $(\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4)$, $(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3)$, $(\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4)$ and Na , K // CO_3 , SO_4 were obtained previously:

$\Delta g_{\text{Na}_2/(\text{CO}_3)(\text{SO}_4)} = 1,106.7 + 1,060.0 Y_{\text{CO}_3}$ (J/mol) [40] (This is a Bragg-Williams type term and Y_{CO_3} is the equivalent site fraction of CO_3)

$$\Delta g_{\text{K}_2/(\text{CO}_3)(\text{SO}_4)} = 1,571.7 + 105.0 Y_{\text{CO}_3}$$
 (J/mol) [40]

$$\Delta g_{\text{NaK}/(\text{CO}_3)_2} = 4,935.0 - 2,928.2 Y_{\text{K}}$$
 (J/mol) [40]

$$\Delta g_{\text{NaK}/(\text{SO}_4)_2} = 3,040.4 + (2,370.9 - 3.1241 \times T) Y_K \text{ (J/mol) [39, 40]}$$

$$\Delta g_{\text{NaK}/(\text{CO}_3)(\text{SO}_4)} = 1,401.3 \text{ (J/mol) [40]}$$

The following CrO_4 -based interaction parameters were obtained in the present work:

$$\Delta g_{\text{Na}_2/(\text{CO}_3)(\text{CrO}_4)} = 8,000.0 - 1,800.0 Y_{\text{CrO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{K}_2/(\text{CO}_3)(\text{CrO}_4)} = 5,600.0 - 800.0 Y_{\text{CrO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{Na}_2/(\text{SO}_4)(\text{CrO}_4)} = 800.0 \text{ (J/mol)}$$

$$\Delta g_{\text{K}_2/(\text{SO}_4)(\text{CrO}_4)} = 1,000.0 - 500.0 Y_{\text{SO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{NaK}/(\text{CrO}_4)_2} = 2,700.0 + (2,000.0 - 2.4500 \times T) Y_K \text{ (J/mol)}$$

Solid solution oS28

Orthorhombic low-temperature allotropes $\text{Na}_2\text{CrO}_{4(\text{S1})}$ and $\text{Na}_2\text{SO}_{4(\text{S1})}$ mutually soluble, and dissolving K_2CrO_4 , Na_2CO_3 , K_2SO_4 and K_2CO_3

Cmcm space group

Sublattice structure: $(\text{Na}^+, \text{K}^+)_2(\text{SO}_4^{2-}, \text{CrO}_4^{2-}, \text{CO}_3^{2-})$

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

$$g_{\text{Na}_2\text{CrO}_4}^\circ = g_{\text{Na}_2\text{CrO}_{4(\text{S1})}}^\circ$$

$$g_{\text{Na}_2\text{SO}_4}^\circ = g_{\text{Na}_2\text{SO}_{4(\text{S1})}}^\circ$$

$$g_{\text{Na}_2\text{CO}_3}^\circ = g_{\text{Na}_2\text{CO}_{3(\text{S2})}}^\circ + 7,112.8 \text{ (J/mol) [40]}$$

$$g_{\text{K}_2\text{CrO}_4}^\circ = g_{\text{K}_2\text{CrO}_{4(\text{S1})}}^\circ + (33,472.0 - 7.7404 \times T) \text{ (J/mol)}$$

$$g_{\text{K}_2\text{SO}_4}^\circ = g_{\text{K}_2\text{SO}_{4(\text{S1})}}^\circ + 33,472.0 \text{ (J/mol) [40]}$$

$$g_{\text{K}_2\text{CO}_3}^\circ = g_{\text{K}_2\text{CO}_{3(\text{S1})}}^\circ + 4,184.0 \text{ (J/mol) [40]}$$

The following Redlich-Kister interaction parameter for $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4)$ was obtained previously:

$$L_{\text{Na}/(\text{CO}_3)(\text{SO}_4)}^0 = 3,347.2 \text{ (J/mol) [40]}$$

The following CrO_4 -based Redlich-Kister interaction parameters were obtained in the present work:

$$L_{\text{Na}/(\text{CrO}_4)(\text{CO}_3)}^0 = 100,000.0 \text{ (J/mol)}$$

$$L_{\text{Na}/(\text{CrO}_4)(\text{SO}_4)}^0 = 3,000.0 \text{ (J/mol)}$$

Solid solution oP28

Orthorhombic low-temperature allotropes $\text{K}_2\text{CrO}_{4(\text{S1})}$ and $\text{K}_2\text{SO}_{4(\text{S1})}$ mutually soluble, and dissolving Na_2CrO_4 , K_2CO_3 , Na_2SO_4 and Na_2CO_3

Pnma space group

Sublattice structure: $(\text{K}^+, \text{Na}^+)_2(\text{SO}_4^{2-}, \text{CrO}_4^{2-}, \text{CO}_3^{2-})$

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

$$g_{\text{K}_2\text{CrO}_4}^\circ = g_{\text{K}_2\text{CrO}_{4(\text{S1})}}^\circ$$

$$g_{\text{K}_2\text{SO}_4}^\circ = g_{\text{K}_2\text{SO}_{4(\text{S1})}}^\circ$$

$$g_{\text{K}_2\text{CO}_3}^\circ = g_{\text{K}_2\text{CO}_{3(\text{S1})}}^\circ + 209.2 \text{ (J/mol) [40]}$$

$$g_{\text{Na}_2\text{CrO}_4}^\circ = g_{\text{Na}_2\text{CrO}_{4(\text{S1})}}^\circ + (13,388.8 + 2.7196 \times T) \text{ (J/mol)}$$

$$g_{\text{Na}_2\text{SO}_4}^\circ = g_{\text{Na}_2\text{SO}_{4(\text{S1})}}^\circ + (29,288.0 - 20.9200 \times T) \text{ (J/mol) [40]}$$

$$g_{\text{Na}_2\text{CO}_3}^\circ = g_{\text{Na}_2\text{CO}_{3(\text{S1})}}^\circ + 20,920.0 \text{ (J/mol) [40]}$$

The following Redlich-Kister interaction parameters for $(\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4)$ were obtained previously:

$$L_{\text{K}/(\text{CO}_3)(\text{SO}_4)}^0 = 3,765.6 \text{ (J/mol) [40]}$$

$$L_{\text{K}/(\text{CO}_3)(\text{SO}_4)}^1 = -2,008.3 \text{ (J/mol) [40]}$$

The following CrO_4 -based Redlich-Kister interaction parameters were obtained in the present work:

$$L_{K/(CO_3)(CrO_4)}^0 = 17,500.0 \text{ (J/mol)}$$

$$L_{K/(CO_3)(CrO_4)}^1 = 3,000.0 \text{ (J/mol)}$$

$$L_{K/(CrO_4)(SO_4)}^0 = 1,800.0 \text{ (J/mol)}$$

Glaserite solid solution hP14

Solid $K_3Na(SO_4)_2$ and $K_3Na(CrO_4)_2$ mutually soluble, and dissolving Na^+

$P\bar{3}m1$ space group

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

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

$$g_{K_3Na(SO_4)_2}^\circ = 1.5 \times g_{K_2SO_4(S1)}^\circ + 0.5 \times g_{Na_2SO_4(S2)}^\circ - 10,878.4 + 9.7906 \times T \text{ (J/mol) [39]}$$

$$g_{Na_3Na(SO_4)_2}^\circ = 2 \times g_{Na_2SO_4(S2)}^\circ + 16,736.0 - 10.7110 \times T \text{ (J/mol) [39]}$$

$$g_{K_3Na(CrO_4)_2}^\circ = 1.5 \times g_{K_2CrO_4(S1)}^\circ + 0.5 \times g_{Na_2CrO_4(S1)}^\circ - 17,154.4 + 9.4140 \times T \text{ (J/mol)}$$

$$g_{Na_3Na(CrO_4)_2}^\circ = 2 \times g_{Na_2CrO_4(S1)}^\circ + 12,970.4 - 8.1588 \times T \text{ (J/mol)}$$

Solid solution oF56

Orthorhombic low-temperature allotrope $Na_2SO_{4(S3)}$ dissolving Na_2CrO_4 , K_2SO_4 and K_2CrO_4

Fddd space group

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

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

$$g_{Na_2SO_4}^\circ = g_{Na_2SO_{4(S3)}}^\circ$$

$$g_{K_2SO_4}^\circ = g_{K_2SO_{4(S1)}}^\circ + 66,944.0 \text{ (J/mol)}$$

$$g_{Na_2CrO_4}^\circ = g_{Na_2CrO_{4(S1)}}^\circ + 4,100.3 \text{ (J/mol)}$$

$$g_{K_2CrO_4}^* = g_{K_2CrO_{4(S1)}}^\circ + 66,944.0 \text{ (J/mol)}$$

Solid solution aP22

Triclinic allotropes $\text{Na}_2\text{S}_2\text{O}_7$ and $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S}2)}$ mutually soluble, and dissolving $\text{K}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7$

$A\bar{1}$ space group

Sublattice structure: $(\text{Na}^+, \text{K}^+)_2(\text{S}_2\text{O}_7^{2-}, \text{Cr}_2\text{O}_7^{2-})$

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

$$g_{\text{Na}_2\text{S}_2\text{O}_7}^\circ = g_{\text{Na}_2\text{S}_2\text{O}_{7(\text{S})}}^\circ$$

$$g_{\text{K}_2\text{S}_2\text{O}_7}^\circ = g_{\text{K}_2\text{S}_2\text{O}_{7(\text{S}2)}}^\circ + 29,288.0 \text{ (J/mol) [39]}$$

$$g_{\text{Na}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S}2)}}^\circ$$

$$g_{\text{K}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}2)}}^\circ + 7,531.2 + 5.6484 \times T \text{ (J/mol)}$$

Solid solution aP44

Triclinic low-temperature allotropes $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S}1)}$ and $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}1)}$ mutually soluble

$P\bar{1}$ space group

Sublattice structure: $(\text{Na}^+, \text{K}^+)_2(\text{Cr}_2\text{O}_7^{2-})$

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

$$g_{\text{Na}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S}1)}}^\circ$$

$$g_{\text{K}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}1)}}^\circ$$

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

$$L_{\text{NaK/Cr}_2\text{O}_7}^0 = 20,000.0 \text{ (J/mol)}$$

Solid solution $\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s})$

Monoclinic high-temperature allotrope $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}2)}$ dissolving $\text{Na}_2\text{Cr}_2\text{O}_7$

$P2_1/c$ space group

Sublattice structure: $(\text{K}^+, \text{Na}^+)_2(\text{Cr}_2\text{O}_7^{2-})$

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

$$g_{\text{K}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{K}_2\text{Cr}_2\text{O}_{7(\text{S}2)}}^\circ$$

$$g_{\text{Na}_2\text{Cr}_2\text{O}_7}^{\circ} = g_{\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_2)}^{\circ} + 11,296.8 + 3.8911 \times T \text{ (J/mol)}$$

Rocksalt solid solution cF8

Cubic NaCl and KCl mutually soluble

Fm $\bar{3}$ m space group

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

$$g_{\text{NaCl}}^{\circ} = g_{\text{NaCl}(\text{S})}^{\circ}$$

$$g_{\text{KCl}}^{\circ} = g_{\text{KCl}(\text{S})}^{\circ}$$

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

$$L_{\text{NaK/Cl}}^0 = 15,972.0 + 32.7960 \times T - 5.5930 \times T \times \ln(T) \text{ (J/mol) [237]}$$

$$L_{\text{NaK/Cl}}^1 = 1,639.0 \text{ (J/mol) [237]}$$

* The "end-member" K₂CrO₄ was added to the oF56 solid solution. Its Gibbs energy in the hypothetical orthorhombic / Fddd crystal structure is that of K₂CrO₄(S₁) augmented by a positive Gibbs energy. The latter was assumed to be identical to that for the "end-member" K₂SO₄ (that is, 66,944.0 J/mol), which was previously obtained by Lindberg et al in an unpublished work. The "end-member" K₂CrO₄ is only required for calculations in the Na, K // SO₄, CrO₄ ternary reciprocal system and higher-order systems.

7.5 Experimental procedure

7.5.1 DSC-TGA

Materials and measurements

In this study, high purity gases (99.999% pure Ar and 99.999% pure CO₂) from Oy Linde Gas AB (Finland) were used, along with the initial reagents KCl, Na₂CO₃, K₂CO₃, Na₂CrO₄·4H₂O, and K₂CrO₄. The supplier's name, CAS number, and purity of each solid reagent are given in Table 7.5.

Table 7.5 Purity and origin of the solid reagents used in our experiments

Chemical formula	Supplier	CAS number	Purity (%)
KCl	Sigma-Aldrich	7447-40-7	≥ 99.0
Na ₂ CO ₃	Sigma-Aldrich	497-19-8	≥ 99.95
K ₂ CO ₃	Sigma-Aldrich	584-08-7	99.995
Na ₂ CrO ₄ ·4H ₂ O	Sigma-Aldrich	10034-82-9	99.0
K ₂ CrO ₄	Alfa-Aesar	7789-00-6	99.9

A NETZSCH STA 449 F1 Jupiter® simultaneous DSC-TGA apparatus was used to perform experiments in relevant binary sub-systems, specifically in (Na₂CO₃ + Na₂CrO₄), (K₂CO₃ + K₂CrO₄), and (Na₂CrO₄ + K₂CrO₄), at compositions where experimental phase diagram data were lacking in the literature. In addition, the ternary common-cation mixture (55.0 mol% KCl + 28.0 mol% K₂CO₃ + 17.0 mol% K₂CrO₄) was investigated to confirm the characteristics of the ternary eutectic predicted by our model.

The calibration of the DSC apparatus is described in [31]. The experimental error for the temperatures was estimated to be $\pm 1^\circ\text{C}$. A dehydration treatment of all pure compounds was performed prior to the DSC-TGA measurements. All reagents were heated in a Vulcan oven (model: 3-130) for 3 hours at 200°C, with the aim of removing water absorbed by the samples during their storage, as well as most of the water present in the initial Na₂CrO₄·4H₂O reagent. Once the treatment was completed, the reagents were allowed to cool down to 25°C.

For measurements in the two common-cation binary sub-systems (Na₂CO₃ + Na₂CrO₄) and (K₂CO₃ + K₂CrO₄) and the common-cation ternary sub-system (KCl + K₂CO₃ + K₂CrO₄), 15-20 mg of the dehydrated binary or ternary mixtures were placed in a Pt/Rh (80/20) crucible. Flow rates of 90 ml/min CO₂ and 10 ml/min Ar were used as the shielding gas for all runs. It should be noted that

the use of a saturated CO_2 gas atmosphere was intended to avoid dissociation of Na_2CO_3 and K_2CO_3 at high temperatures into $\text{Na}_2\text{O}_{(\text{s})}$ and $\text{CO}_{2(\text{g})}$, and $\text{K}_2\text{O}_{(\text{s})}$ and $\text{CO}_{2(\text{g})}$ and/or partial volatilization. On the other hand, a flow rate of 70 ml/min Ar was employed as the shielding gas for all runs related to the $(\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4)$ common-anion binary sub-system. All DSC-TGA experiments performed in the present work are reported in the Supporting Information (Appendix C, see Tables C1 to C5).

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 $10^\circ\text{C}/\text{min}$.

The temperature range investigated was carefully selected for each binary or ternary composition, with the maximum temperature set at 49°C above the estimated liquidus temperature and the minimum temperature at least 50°C below the temperature of the first solid-solid transition. A holding time of one minute was used in each case. The maximum temperature was kept low enough to minimize vaporization but high enough to ensure complete melting. To monitor any mass loss or volatilization, thermogravimetric analysis (TGA) was carried out. Throughout the experiments, mass loss and heat flux were continuously measured, with a maximum mass loss target of 3%. The overall mass loss for each binary or ternary composition investigated was determined at the end of each DSC-TGA experiment and is reported in the Supporting Information (Tables C1 to C5).

Usually, only heating runs were considered. Each solid-solid transition was defined as the temperature at the onset of the peak, whereas each liquidus temperature and eutectic temperature was defined as the temperature at the maximum of the peak [238].

To avoid including non-reproducible data resulting from the thermal history of the sample, the first heating/cooling cycle was almost systematically excluded from our analysis. Nevertheless, for the four equilibrated chrome-glaserite compositions studied in this work (Table C4 in the Supporting Information), the first heating/cooling cycle was included in our analysis since the corresponding

samples had undergone a three-week equilibration at 400°C.

In this paper, for each binary common-ion sub-system investigated experimentally, a DSC thermogram related to a specific composition is displayed.

To perform the equilibration process of the chrome-glaserite phase, a mixture of pre-treated pure powders of K_2CrO_4 and $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ was mechanically mixed at the stoichiometric composition of (45 mol% Na_2CrO_4 + 55 mol% K_2CrO_4). This mixture was sealed in a fused silica tube and heated from room temperature to 800°C for 50 minutes at a heating rate of 15°C/min. The sample was then cooled to 400°C for 27 minutes at a cooling rate of 15°C/min in a muffle furnace. After annealing at 400°C for three weeks under Ar at a flow rate of approximately 1 ml/min, the equilibrated sample was cooled using liquid nitrogen, mechanically ground, and then analyzed by SEM-EDS and DSC-TGA.

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

The equilibrated chrome-glaserite sample (solid solution of 45 mol% Na_2CrO_4 + 55 mol% K_2CrO_4) after quenching was analyzed at room temperature with a LEO 1450 (Carl Zeiss Microscopy GmbH, Jena, Germany) scanning electron microscope (SEM) coupled with an Oxford Instruments X-Max 50 mm² (Oxford Instruments plc, Abingdon, Oxfordshire, UK) energy dispersive spectrometer (EDS).

The analysis by SEM-EDS confirmed the global homogeneity of the chrome-glaserite phase. Twenty EDS analyses were performed to confirm the formation of the phase, and six selected analysis results are presented in Table 7.6 with an estimated experimental error of $\pm 5\%$. The estimated composition of the equilibrated chrome-glaserite phase is $\text{Na}_{1.03}\text{K}_{1.13}\text{Cr}_{1.05}\text{O}_{3.92}$, whereas the original mechanical mixture had the composition $\text{Na}_{0.9}\text{K}_{1.1}\text{CrO}_4$.

Table 7.6 EDS analysis results of selected spectra for the quenched chrome-glaserite sample with an estimated experimental error of $\pm 5\%$

Element	Spectrum 1	Spectrum 2	Spectrum 5	Spectrum 6	Spectrum 12	Spectrum 17	Average
O	3.847	4.058	3.982	3.890	3.841	3.920	3.923
Na	1.000	1.056	1.000	1.000	1.013	1.097	1.028
K	1.222	1.101	1.093	1.216	1.090	1.075	1.133
Cr	1.157	1.000	1.008	1.108	1.000	1.000	1.045
K / (Na + K)	0.550	0.510	0.522	0.549	0.518	0.495	0.524
(Na + K) / Cr	1.920	2.157	2.076	2.000	2.103	2.172	2.068

7.6 Chromate-based common-ion binary sub-systems

This section presents all CrO_4 -based and Cr_2O_7 -based common-ion binary sub-systems for which thermodynamic data (mainly phase equilibria) were available. All phase diagrams were calculated in air ($p(\text{O}_2) = 0.21 \text{ atm}$). The gas phase was assumed ideal, and the gaseous species considered for the calculations were C, C_2 , C_3 , C_4 , C_5 , O, O_2 , O_3 , CO, C_2O , CO_2 , C_3O_2 , Na, Na_2 , NaO, S, S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , S_8 , CS, CS_2 , SO, SO_2 , SO_3 , SSO, COS, Na_2SO_4 , Cl, Cl_2 , CCl, C_2Cl , CCl_2 , C_2Cl_2 , CCl_3 , C_2Cl_3 , CCl_4 , C_2Cl_4 , C_2Cl_5 , C_2Cl_6 , C_6Cl_6 , ClO, ClO_2 , ClO_3 , Cl_2O , ClOOCl , ClOClO , ClClOO , COCl , COCl_2 , NaCl, $(\text{NaCl})_2$, SCl, S_2Cl , SCl_2 , ClSSCl , SOCl_2 , SO_2Cl_2 , K, K_2 , KO, K_2SO_4 , KCl, $(\text{KCl})_2$, Cr, CrO, CrO_2 , CrO_3 , CrS, CrCl, CrCl_2 , CrCl_3 , CrCl_4 , CrCl_5 , CrCl_6 , CrOCl , CrO_2Cl , CrOCl_2 , CrO_2Cl_2 , CrOCl_3 , and CrOCl_4 . These were all taken from the FactPS database in FactSage [42]. Also, the possible reactions $2 \text{A}_2\text{CrO}_4 = \text{A}_2\text{Cr}_2\text{O}_7 + \text{A}_2\text{O}$ (where A = Na, K) were considered in the calculated phase diagrams for all CrO_4 -based binary sub-systems, but those reactions are very limited up to above the liquidus temperatures [34].

7.6.1 The (NaCl + Na₂CrO₄) system

The phase diagram has been investigated using various techniques [117, 124, 239]. Sackur [239] employed the method of cooling curves to measure the liquidus temperature of four NaCl-rich mixtures. Rasninskaya and Bergman [117], and Shinata [124] used the visual-polythermal technique and differential thermal analysis (DTA), respectively. (NaCl + Na₂CrO₄) is a simple eutectic-type binary system with no reported solid solutions or intermediate compounds. The measured limiting slopes of the NaCl and Na₂CrO₄ liquidus curves at $x(\text{NaCl}) = 1$ and $x(\text{Na}_2\text{CrO}_4) = 1$ respect the limiting liquidus slope equation (7.16), which assumes no solid solubility :

$$\left(\frac{dT}{dx_m^{\text{liquidus}}} \right) = \frac{RT_{\text{fusion}(m)}^2}{\Delta h_{\text{fusion}(m)}^\circ} \text{ at } [x_m = 1] \quad (7.16)$$

where $\Delta h_{\text{fusion}}^\circ$ and T_{fusion} are, respectively, the enthalpy and temperature of fusion of the pure salt m.

The measurements of Shinata [124] are somewhat scattered. The liquidus data of Rasninskaya and Bergman [117] are satisfactorily reproduced by our model. Rasninskaya and Bergman [117] reported a eutectic at 54.4 mol% Na₂CrO₄ and 572°C whereas Shinata [124] reported a eutectic temperature of 576.9°C. The calculated characteristics of the eutectic are 54.4 mol% Na₂CrO₄ and 573°C.

The thermal arrest observed by Shinata [124] at about 419°C corresponds to the solid-solid transition Na₂CrO₄(S1) = Na₂CrO₄(S2).

The calculated (NaCl + Na₂CrO₄) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is shown along with the measurements in Figure 7.1.

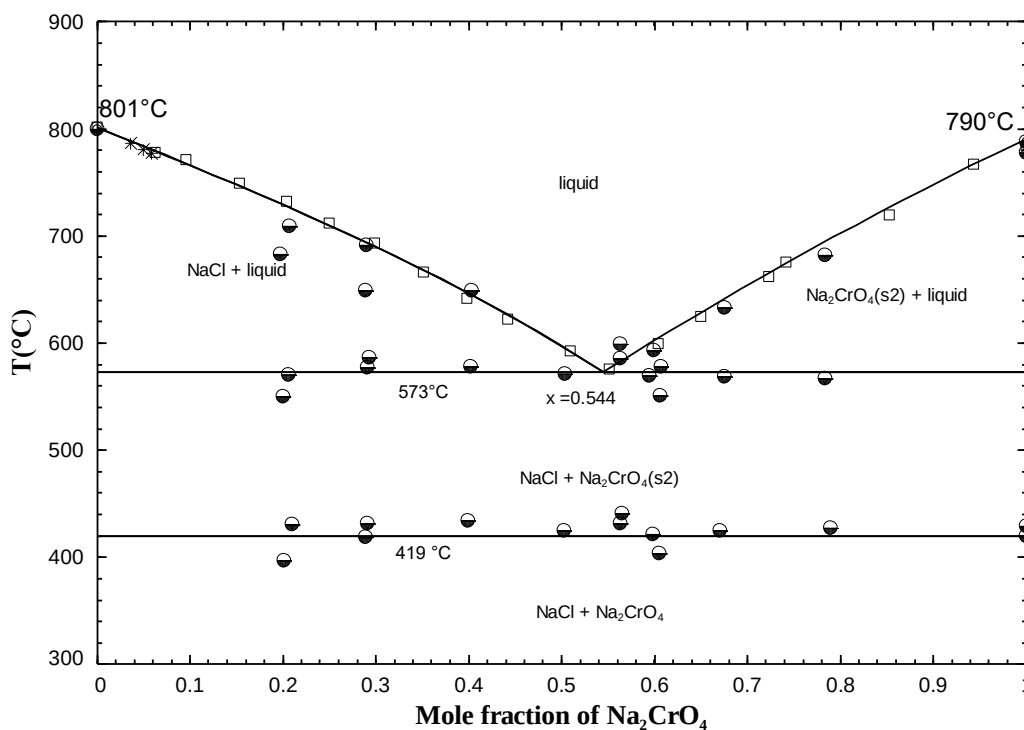


Figure 7.1 Calculated (NaCl + Na₂CrO₄) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Sackur [239] (*), Rasnonskaya and Bergman [117] (□), and Shinata [124] (⊙)

7.6.2 The (KCl + K₂CrO₄) system

The phase diagram has been measured by the method of cooling curves [132, 239], and the visual-polythermal method in a platinum crucible [240, 241]. (KCl + K₂CrO₄) is a simple eutectic system with no reported solid solutions or intermediate compounds. The measured limiting slope of the KCl liquidus curve agrees with equation (7.16).

The liquidus temperatures for KCl-rich compositions measured by Rasnonskaya and Bergman [240, 241], and Sackur [239] are in good agreement. It was not possible to reproduce the data of Żemczużny [132] near the pure compounds since their melting points reported by Żemczużny are higher than the values selected in the present work [31, 42]. In particular, for pure KCl, this author measured a temperature of fusion more than 20°C higher than the accepted value of 771°C.

For compositions near the eutectic point, the liquidus temperatures of [132] and [240, 241] are in

reasonable agreement. Żemczużny [132] reported a eutectic at 31.5 mol% K_2CrO_4 and 658°C , while Rassonskaya and Bergman [240, 241] reported a somewhat lower eutectic temperature of 650°C at the same composition. The calculated characteristics of the eutectic are 32.1 mol% K_2CrO_4 and 651°C .

The binary liquid was assumed to be ideal (that is, $\Delta g_{\text{K}_2/(\text{Cl})(\text{CrO}_4)} = 0$). This is consistent with the fact that the $(\text{NaCl} + \text{Na}_2\text{CrO}_4)$ liquid is relatively close to ideal (see model parameters in Table 7.3).

The calculated $(\text{KCl} + \text{K}_2\text{CrO}_4)$ phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 7.2.

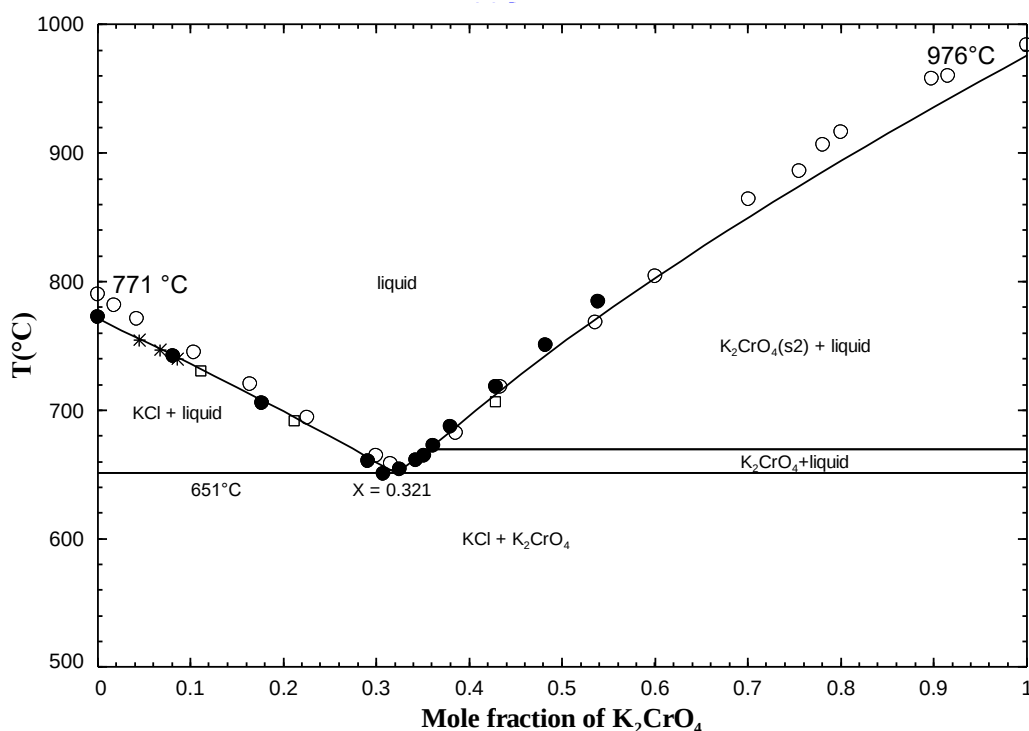


Figure 7.2 Calculated $(\text{KCl} + \text{K}_2\text{CrO}_4)$ phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Żemczużny [132] ($\circ$), Sackur [239] ($*$), and Rassonskaya and Bergman [240, 241] ($\bullet$, $\square$)

7.6.3 The ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4$) system

The phase diagram has been measured by the method of cooling curves [118, 242] and DTA [125].

In the present work, DSC-TGA measurements were performed for several binary mixtures with various contents of Na_2CrO_4 : 5 and 10 mol% (from 250 to 865°C), and 90, 92.5 and 95 mol% (from 250 to 800°C). As an example, the DSC thermogram for the binary composition (90 mol% $\text{Na}_2\text{CO}_3 + 10 \text{ mol% Na}_2\text{CrO}_4$) is shown in Figure 7.3.

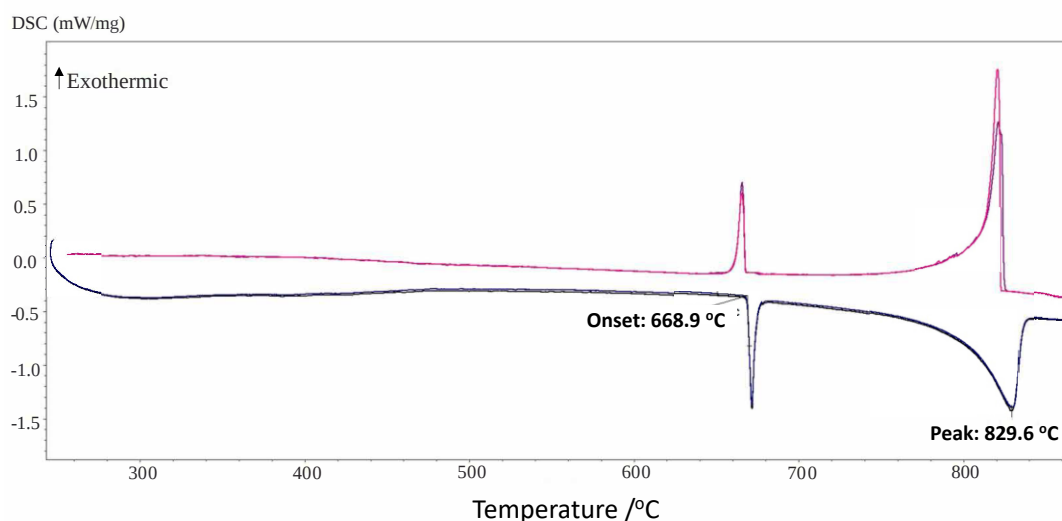


Figure 7.3 DSC thermogram for the mixture (90 mol% $\text{Na}_2\text{CO}_3 + 10 \text{ mol% Na}_2\text{CrO}_4$) (2nd and 3rd heating/cooling cycles only)

According to the studies of [118, 125], there is a eutectic at 52.0 mol% Na_2CrO_4 and 654°C. The calculated characteristics of the eutectic are 53.8 mol% Na_2CrO_4 and 649°C. The high-temperature allotropes $\text{Na}_2\text{CO}_{3(\text{S}3)}$ and $\text{Na}_2\text{CrO}_{4(\text{S}2)}$ have the same hexagonal crystal structure and space group $\text{P6}_3/\text{mmc}$ (see Table 7.1). Therefore, the experimental eutectic plateau observed over a wide composition range can be attributed to a miscibility gap, with the presence of two solid solutions having the same crystal structure (hP22) and different compositions. The measurements of Tathavadkar et al [125], which report a eutectic plateau from 6.0 to 86.8 mol% Na_2CrO_4 , were favored in the present work. The calculated solid solubility limits are 6.2 and 86.6 mol% Na_2CrO_4 , respectively. Note that the true solid solubility limits may be somewhat lower than the values suggested by the measurements of Tathavadkar et al [125]. However, as seen in Figure 7.4, all

available data points are reasonably well reproduced by our model. No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the liquid phase. The latter displays small positive deviations from ideality (see Table 7.3). The ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4$) common-cation binary liquid was expected to be close to ideal owing to the close similarity of the anionic radii (2.10 Å for CO_3^{2-} , and 2.32 Å for CrO_4^{2-} [243]).

In our DSC thermograms for Na_2CrO_4 -rich compositions, a thermal arrest was observed around 360°C both upon heating and cooling. This is attributed to the solid-solid transition $\text{Na}_2\text{CO}_{3(\text{S1})} = \text{Na}_2\text{CO}_{3(\text{S2})}$, which occurs at 358.9°C [40]. Thus, 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 Na_2CO_3 in the low-temperature allotrope $\text{Na}_2\text{CrO}_{4(\text{S1})}$ (see Table 7.4). In our DSC thermograms for Na_2CO_3 -rich compositions, no signals were detected at low temperatures.

The calculated ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21$ atm) is shown along with the measurements in Figure 7.4. The calculated isobar at 1 atm is displayed in this figure and shows that $\text{Na}_2\text{CO}_{3(\text{S3})}$ partly decomposes to form liquid Na_2O (dissolved in the molten salt phase) and $\text{CO}_2(\text{g})$. However, this decomposition is calculated to be extremely limited (mole fraction of Na_2O of the order of 10^{-9}). As reported previously, such a decomposition was avoided in our DSC-TGA measurements thanks to the use of a $\text{CO}_2(\text{g})$ saturated atmosphere.

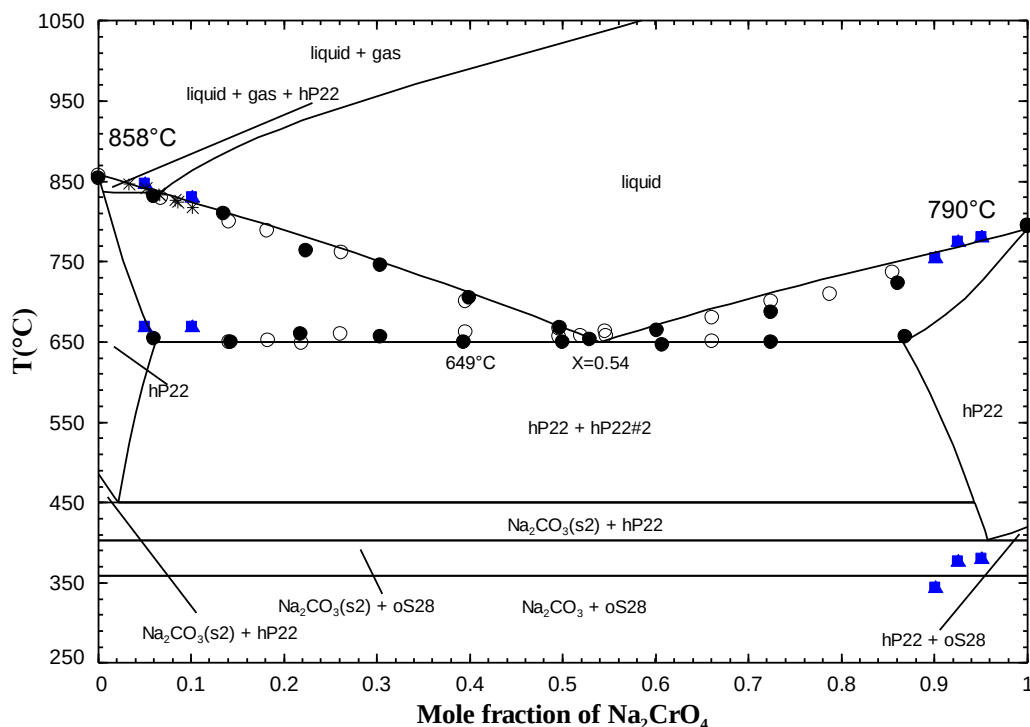


Figure 7.4 Calculated ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Sackur [242] (*), Vilnyanski and Pudovkina [118] (○), Tathavadkar et al [125] (●) and this work (blue symbols) (DSC, 2nd heating : ▲ , 3rd heating : ■)

7.6.4 The ($\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4$) system

The phase diagram has been measured by the method of cooling curves [242, 244] and the visual-polythermal technique [245]. Sackur [242] only studied K_2CO_3 -rich mixtures. Kurnakov and Shemtshushny [244] reported a continuous series of solid solutions with a minimum at 33.0 mol% K_2CrO_4 and 806°C, while Sanzharov and Bergman [245] observed an extensive solid solution with a marked minimum at 36.0 mol% K_2CrO_4 and 788°C.

In the present work, DSC-TGA measurements were performed for several binary mixtures with various contents of K_2CrO_4 : 40 and 60 mol% (from 300 to 870°C), and 80 and 90 mol% (from 300 to 960°C). As an example, the DSC thermogram for the binary composition (10 mol% $\text{K}_2\text{CO}_3 + 90 \text{ mol\% K}_2\text{CrO}_4$) is displayed in Figure 7.5.

The high-temperature allotropes $\text{K}_2\text{CO}_3(\text{s}_2)$ and $\text{K}_2\text{CrO}_4(\text{s}_2)$ have the same hexagonal crystal structure and space group $\text{P6}_3/\text{mmc}$ (Table 7.1), and therefore a high-temperature solid solution (hP22) was introduced over the entire composition range. A minimum was calculated at 38.7 mol% K_2CrO_4 and 807°C. The latter temperature agrees very well with that reported by Kurnakov and Shemtshushny [244]. Overall, all liquidus and solidus data are reasonably well reproduced by our model (Figure 7.6). At low temperatures, a miscibility gap (related to the hP22 solid solution) was calculated and agreed well with our low-temperature thermal arrests at 40 and 60 mol% K_2CrO_4 . As was discussed previously, a miscibility gap (related to hP22) was also observed experimentally in the $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4)$ phase diagram. Some solid solubility of K_2CO_3 in the low-temperature allotrope $\text{K}_2\text{CrO}_4(\text{s}_1)$ was introduced (see oP28 solid solution in Table 7.4) in order to reproduce our low-temperature thermal arrests at 80 and 90 mol% K_2CrO_4 . For K_2CO_3 -rich binary mixtures, no experimental data were available at low temperatures, and, therefore, this part of the calculated phase diagram was predicted. No experimental data other than phase equilibria were available to calibrate the $(\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ liquid phase. The latter displays small positive deviations from ideality (Table 7.3), as was the case for the $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4)$ liquid. The $(\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ common-cation binary liquid was expected to be close to ideal due to the close similarity of the radii of the CO_3^{2-} and CrO_4^{2-} anions [243].

The calculated $(\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 7.6. According to the calculated isobar at 1 atm shown in this figure, $\text{K}_2\text{CO}_3(\text{s}_2)$ partly decomposes into liquid K_2O (dissolved in the liquid solution) and $\text{CO}_2(\text{g})$. Nevertheless, this decomposition was calculated to be extremely limited (mole fraction of K_2O of the order of 10^{-10}). The use of a $\text{CO}_2(\text{g})$ saturated atmosphere in our DSC-TGA measurements permitted us to avoid such a decomposition.

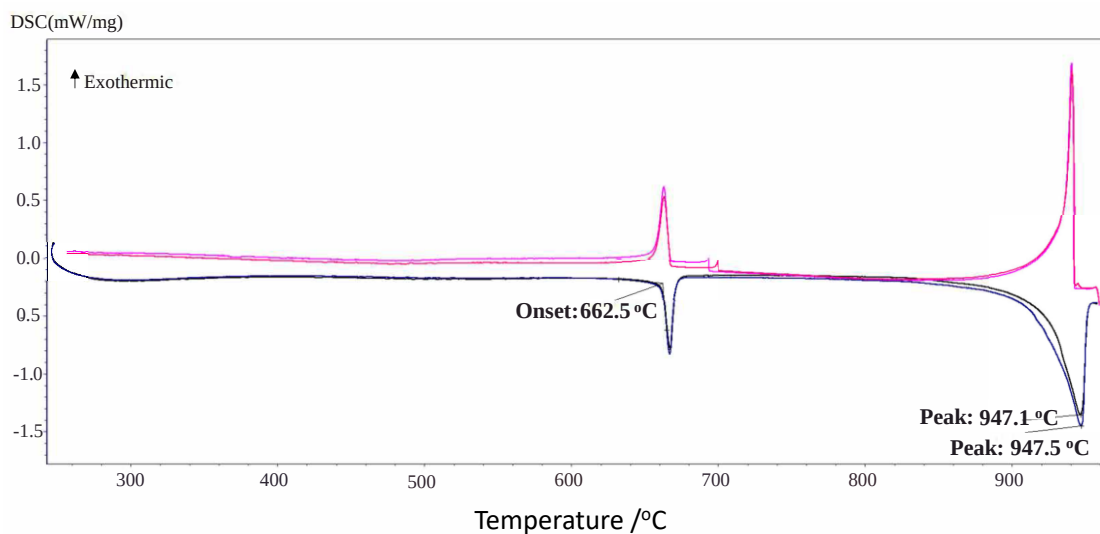


Figure 7.5 DSC thermogram for the mixture (10 mol% K_2CO_3 + 90 mol% K_2CrO_4) (2nd and 3rd heating/cooling cycles only)

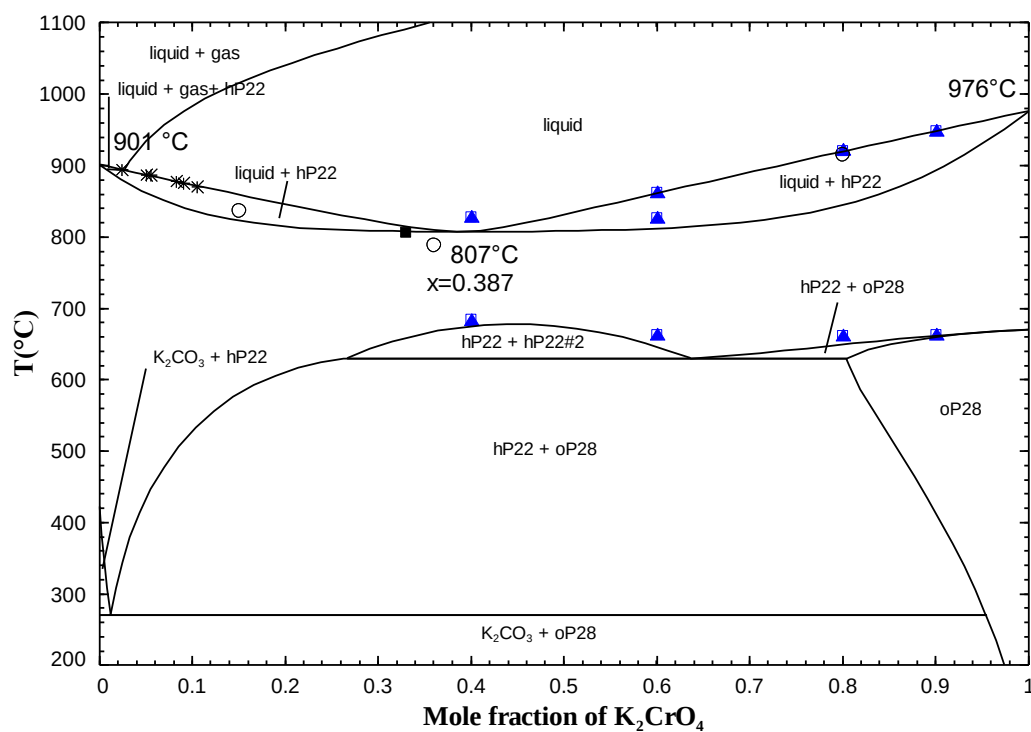


Figure 7.6 Calculated (K_2CO_3 + K_2CrO_4) phase diagram in air ($p(\text{O}_2) = 0.21$ atm). Experimental data from Kurnakov and Shemtshushny [244] (■), Sackur [242] (*), Sanzharov and Bergman [245] (○) and this work (blue symbols) (DSC, 2nd heating : □, 3rd heating : ▲)

7.6.5 The (Na₂SO₄ + Na₂CrO₄) system

Flach [112], Mateiko and Bukhalova [121], and Eysel [90] have measured the phase diagram using the method of cooling curves, the visual-polythermal technique and DTA, respectively. These various data are in agreement (Figure 7.7), and indicate the existence of a solid solution at high temperatures over the entire composition range and with no minimum [90, 112, 121], as well as an extensive solid solution at intermediate temperatures extending from 235°C (for pure Na₂SO₄) to 413°C (for pure Na₂CrO₄) [90, 112, 121]. Na₂SO_{4(S2)} (respectively Na₂SO_{4(S1)}) and Na₂CrO_{4(S2)} (respectively Na₂CrO_{4(S1)}) have the same crystal structure and space group (Table 7.1). Therefore, a high-temperature solid solution (hP22) and a low-temperature solid solution (oS28) were both introduced over the entire composition range.

At very low temperatures, a Na₂SO_{4(S3)}-rich solid solution (oF56) dissolving Na₂CrO₄ was introduced based on the measurements of Eysel [90]. This author reported the existence of two complete solid solutions : a high-temperature one between Na₂SO_{4(S2)} and Na₂CrO_{4(S2)}, and a low-temperature one between Na₂SO_{4(S1)} and Na₂CrO_{4(S1)}. At room temperature, the Na₂SO_{4(S1)}-rich solid solutions were observed to slowly decompose into two different phases : Na₂SO_{4(S3)}-rich solid solutions and Na₂CrO_{4(S1)}-rich solid solutions. The maximum solid solubility in the former was reported to be lower than 5 mol% Na₂CrO₄ at 20°C, based on the evolution of the lattice parameters measured by XRD. The oF56 solid solution was calculated to dissolve 4.73 mol% Na₂CrO₄ at 20°C.

No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the liquid phase. The latter was assumed to be ideal (that is, $\Delta g_{\text{Na}_2/(\text{SO}_4)(\text{CrO}_4)} = 0$) owing to the very close similarity of the anionic radii (2.31 Å for SO₄²⁻, and 2.32 Å for CrO₄²⁻ [243]).

The calculated (Na₂SO₄ + Na₂CrO₄) phase diagram in air ($p(\text{O}_2) = 0.21$ atm) is shown along with the measurements in Figure 7.7.

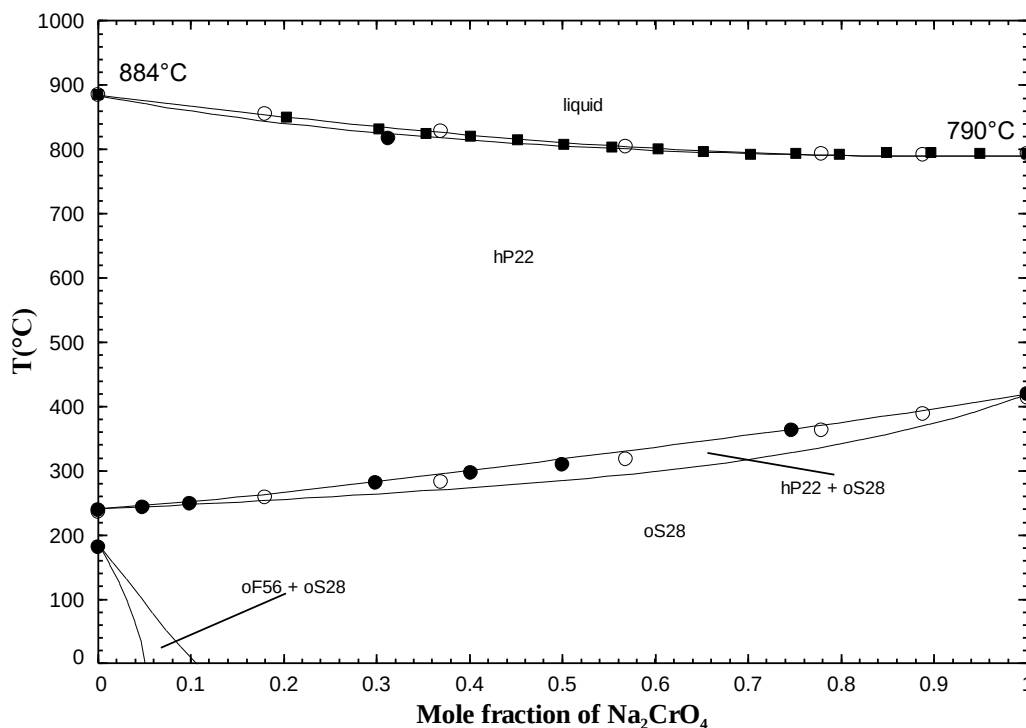


Figure 7.7 Calculated ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Flach [112] ($\circ$), Mateiko and Bukhalova [121] ($\blacksquare$) and Eysel [90] ($\bullet$)

7.6.6 The ($\text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system

The phase diagram has been investigated using various techniques. Using the method of heating and cooling curves, Groschuff [131] reported a continuous series of solid solutions with no maximum or minimum at both high and low temperatures. The method of cooling curves has been employed by Amadori [246]. Eysel [90] performed DTA measurements, which confirmed a close-to-linear crystallization curve at low temperatures between the two pure compounds, as was previously reported by Groschuff [131]. Later studies by Bukhalova and Mateiko [247], and by Sanzharov and Bergman [245], using the visual-polythermal technique, confirmed the high-temperature results of Groschuff [131] and Amadori [246]. Sanzharov and Bergman [245] reported a slight minimum at 80 mol% K_2CrO_4 and 968°C . Finally, visual observations of Le Chatelier [248] revealed the existence of complete solid solutions at both high and low temperatures, which is in agreement with the other studies. $\text{K}_2\text{SO}_{4(\text{S}2)}$ (respectively $\text{K}_2\text{SO}_{4(\text{S}1)}$) and $\text{K}_2\text{CrO}_{4(\text{S}2)}$ (respectively $\text{K}_2\text{CrO}_{4(\text{S}1)}$) have the same crystal structure and space group (Table 7.1). Therefore, a high-

temperature solid solution (hP22) and a low-temperature solid solution (oP28) were both introduced over the entire composition range.

No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the liquid phase. By analogy with the ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$) liquid, the ($\text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) liquid was assumed to be ideal (that is, $\Delta g_{\text{K}_2/(\text{SO}_4)(\text{CrO}_4)} = 0$) owing to the very close similarity of the radii of the SO_4^{2-} and CrO_4^{2-} anions [243].

The calculated ($\text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 7.8.

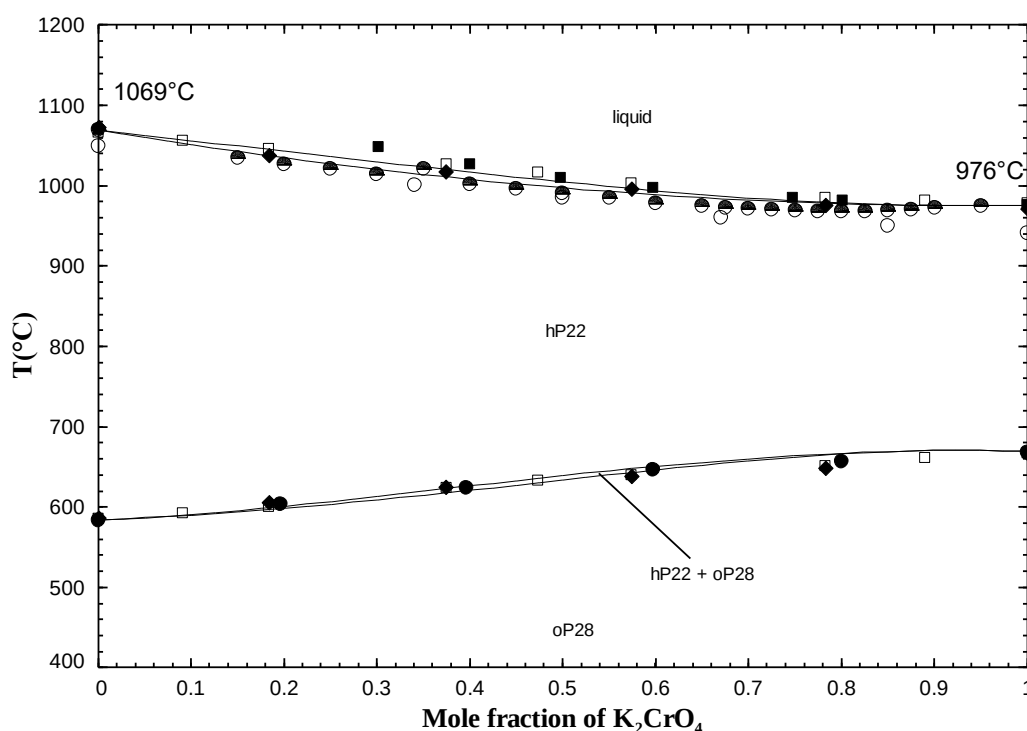


Figure 7.8 Calculated ($\text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Eysel [90] (●), Sanzharov and Bergman [245] (◐), Groschuff [131] (◆), Amadori [246] (□), Bukhalova and Mateiko [247] (■) and Le Chatelier [248] (○). Average temperatures of 624.5, 638.5 and 648.0°C were used in this figure for the temperature ranges of 624-625°C, 637-640°C and 644-652°C reported by [131].

7.6.7 The (Na₂CrO₄ + K₂CrO₄) system

Several studies have been conducted on the (Na₂CrO₄ + K₂CrO₄) binary phase diagram. Flach [112] used the method of cooling curves, while Dergunov and Bergman [136] and Bergman and Vartbaronov [145] used the visual-polythermal technique. These investigations indicated the formation of a complete solid solution at high temperatures, with a minimum at around 30 mol% K₂CrO₄ and 752°C. This can be explained by the fact that the high-temperature allotropes Na₂CrO_{4(s2)} and K₂CrO_{4(s2)} have the same hexagonal crystal structure and space group P6₃/mmc (see Table 7.1). The liquidus and solidus curves measured by Stingele [122] using high-temperature microscopy are reproducible to within 1°C for samples of the same composition, and the minimum reported by [112, 136, 145] has been confirmed. The liquidus curve of Amadori [249] obtained by thermal analysis revealed a minimum at around 25 mol% K₂CrO₄ and 740°C.

Goldberg et al [84] performed powder and single-crystal X-ray diffraction, along with DTA and DSC analyses for samples obtained by melting mixtures of Na₂CrO₄ and K₂CrO₄ and then quenching them in air, or by crystallization from aqueous solutions. Lattice parameters of the quenched samples suggest the formation of two terminal solid solutions based on the low-temperature allotropes Na₂CrO_{4(s1)} and K₂CrO_{4(s1)}. This is consistent with the fact that these are orthorhombic with different space groups (Table 7.1). At intermediate compositions, is reported a trigonal chrome-glaserite phase forming an extended solid solution around the composition NaK₃(CrO₄)₂ and stable at room temperature [84, 90]. Eysel's results [90] suggest that chrome-glaserite should be considered as a solid solution, and that the glaserite phases in the (Na₂CrO₄ + K₂CrO₄) and (Na₂SO₄ + K₂SO₄) systems have close similarities. The chrome-glaserite solid solution exhibits a temperature maximum around the composition (Na_{0.45}K_{0.55})₂CrO₄ and not around NaKCrO₄ [90].

Flach [112] considered the chrome-glaserite phase to be a stoichiometric compound NaK₃(CrO₄)₂, and this author reported no solid solubility in the low-temperature allotropes Na₂CrO_{4(s1)} and K₂CrO_{4(s1)}. He observed a maximum temperature at around 50-55 mol% K₂CrO₄ and 607°C. Amadori [249] reported a flat maximum between 45 and 60 mol% K₂CrO₄ and at 606°C, which was attributed to the formation of the compound Na₂CrO₄.K₂CrO₄ from the high-temperature

hexagonal solid solution (hP22).

Glaserites are solid solutions of the type $(A,C)_2BX_4$, where the A cations include Na^+ , Ag^+ , Mg^{2+} , Ca^{2+} and Cd^{2+} , the C cations include K^+ , Rb^+ , Cs^+ , NH_4^+ , Sr^{2+} , Ba^{2+} and Eu^{2+} , and the tetrahedral complex anions BX_4 include BeF_4^{2-} , SO_4^{2-} , SeO_4^{2-} , CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} , PO_4^{3-} , VO_4^{3-} , AsO_4^{3-} , SiO_4^{4-} , and GeO_4^{4-} [90].

The crystal structure and space group of the two reported forms of chrome-glaserite $K_3Na(CrO_4)_2$ are given in Table 7.7.

Table 7.7 Crystal structure and space group of chrome-glaserite $K_3Na(CrO_4)_2$

$K_3Na(CrO_4)_2$	Crystal structure	Space group	Pearson Symbol/ Phase Prototype	Reference
Low-temperature form	Monoclinic (stable below -34.15°C)	C2/c	-	[84, 250-252]
High-temperature form	Trigonal (stable above -34.15°C)	$P\bar{3}m1$ (164)	hP14 / $K_3Na(SO_4)_2$	

The calculated $(Na_2CrO_4 + K_2CrO_4)$ phase diagram in air ($p(O_2) = 0.21$ atm) is compared to the measurements in Figure 7.9. This phase diagram displays four different solid solutions: a high-temperature hexagonal solid solution (hP22) existing over the entire composition range, an orthorhombic low-temperature solid solution (oS28) rich in $Na_2CrO_{4(S1)}$ and diluted in K_2CrO_4 , an orthorhombic low-temperature solid solution (oP28) rich in $K_2CrO_{4(S1)}$ and diluted in Na_2CrO_4 , and the non-stoichiometric phase $K_3Na(CrO_4)_2$ (chrome-glaserite, hP14). The low-temperature form of chrome-glaserite was not considered in the present work since it is stable at very low temperatures. These various solid solutions along with the optimized model parameters are described in detail in Table 7.4. As shown in this table, the glaserite phase was modelled with the following sublattice structure : $(K^+, Na^+)_3(Na^+)(SO_4^{2-}, CrO_4^{2-})_2$. The first sublattice is occupied by the two cations Na^+

and K^+ (positions 1a and 2a), the second sublattice is only occupied by the Na^+ cation (position 1b), and the third sublattice is occupied by the SO_4^{2-} and CrO_4^{2-} anions. The sulfur-glaserite phase was modelled previously [39], and the corresponding model parameters were used directly in the present work. Only a trigonal form (space group $P\bar{3}m1$) has been reported [90, 253]. In the present work, to model the chrome-glaserite phase, the two new “end-members” $K_3Na(CrO_4)_2$ and $Na_3Na(CrO_4)_2$ were added in the existing hP14 solid solution. Their Gibbs energies were the only model parameters; no interaction parameters were required in the present work as was already the case for the sulfur-glaserite phase [39].

In this work, DSC-TGA measurements were performed for mechanical mixtures of the pre-treated reagents $Na_2CrO_4 \cdot 4H_2O$ and K_2CrO_4 . Six different binary mixtures with various contents of K_2CrO_4 were studied : 35, 45, 55 and 65 mol% (from 30 to 860°C), and 70 and 75 mol% (from 30 to 890°C). Also, DSC-TGA measurements were conducted for the chrome-glaserite composition of (45 mol% Na_2CrO_4 + 55 mol% K_2CrO_4) equilibrated at 400°C for three weeks, to which an excess of Na_2CrO_4 or K_2CrO_4 was added subsequently. Four binary mixtures with various contents of K_2CrO_4 were investigated under those conditions : 40 and 73 mol% (from 30 to 890°C), and 65 and 72 mol% (from 30 to 920°C). All measured thermal arrests are listed in the Supplementary Information (Tables C3 and C4). As an example, the DSC thermogram for the composition (35 mol% Na_2CrO_4 + 65 mol% K_2CrO_4) of the equilibrated chrome-glaserite sample to which an excess of pre-treated K_2CrO_4 was added is shown in Figure 7.10.

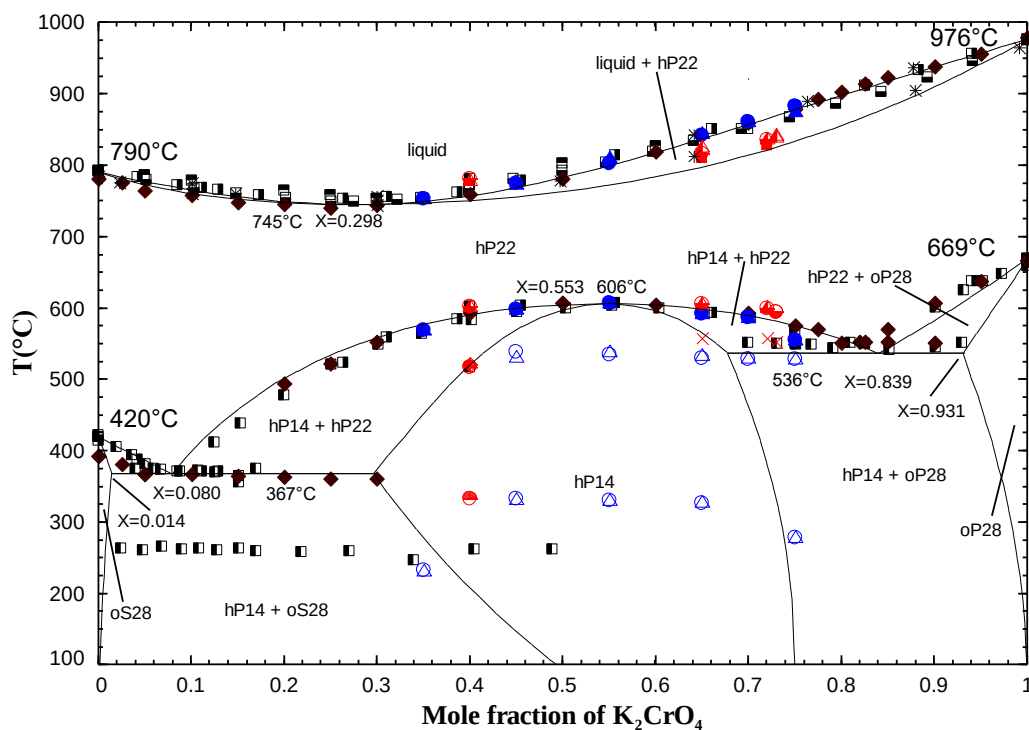


Figure 7.9 Calculated ($\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Flach [112] (■), Amadori [249] (◆), Dergunov and Bergman [136] (■), Bergman and Vartbaronov [145] (■), Stingeles [122] (*), Goldberg et al [84] (■) and this work (blue and red symbols) (DSC, red ■ : 1st heating for chrome-glaserite equilibrated at 400°C for 3 weeks, red × : very low intensity peak of 1st heating for chrome-glaserite equilibrated at 400°C for 3 weeks, blue ● : 2nd heating for mechanical mixtures of pre-treated reagents, blue ○ : very low intensity peak of 2nd heating for mechanical mixtures of pre-treated reagents, red ⊖ : 2nd heating for chrome-glaserite equilibrated at 400°C for 3 weeks, red ⊕ : very low intensity peak of 2nd heating for chrome-glaserite equilibrated at 400°C for 3 weeks, blue ▲ : 3rd heating for mechanical mixtures of pre-treated reagents, blue △ : very low intensity peak of 3rd heating for mechanical mixtures of pre-treated reagents, red ▲ : 3rd heating for chrome-glaserite equilibrated at 400°C for 3 weeks, red ◆ : very low intensity peak of 3rd heating for chrome-glaserite equilibrated at 400°C for 3 weeks)

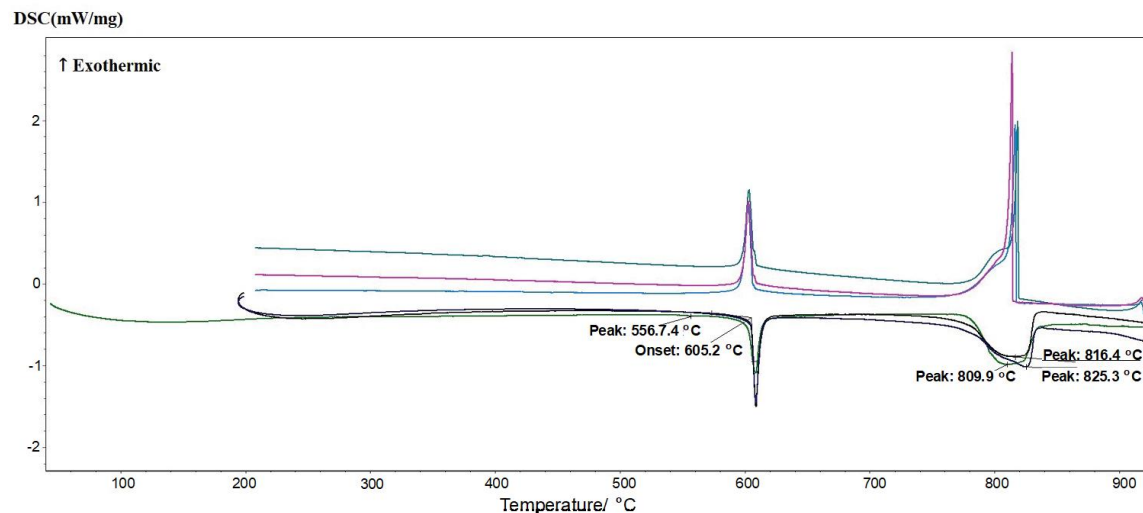


Figure 7.10 DSC thermogram for the composition (35 mol% Na_2CrO_4 + 65 mol% K_2CrO_4) of the equilibrated chrome-glaserite sample to which an excess of pre-treated K_2CrO_4 was added subsequently (1st, 2nd, and 3rd heating/cooling cycles). The temperature value of 556.7°C for the first heating run was taken at the maximum of the peak (and not at the onset of the peak) since this was a very low intensity peak.

No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the (Na_2CrO_4 + K_2CrO_4) liquid phase. Finally, a constant parameter of -1,419.6 J/mol was used by analogy with the (Na_2SO_4 + K_2SO_4) liquid phase, which was previously modeled by Lindberg et al [39]. This parameter had been used to reproduce the enthalpy of mixing data. Note that the SO_4^{2-} and CrO_4^{2-} anions have very similar radii [243]. Then, the hexagonal solid solution (hP22) was modelled in order to best reproduce the high-temperature measurements, in particular the minimum of hP22 (around 30 mol% K_2CrO_4 [112, 122, 136, 145]) and the maximum extension of the chrome-glaserite phase (hP14) at about 605°C [84]. Three model parameters were required for hP22. The Gibbs energies of the two “end-members” $\text{K}_3\text{Na}(\text{CrO}_4)_2$ and $\text{Na}_3\text{Na}(\text{CrO}_4)_2$ in hP14 were optimized simultaneously. Finally, the two low-temperature terminal solid solutions (oS28 and oP28) were modelled in order to best reproduce the experimental temperatures and compositions of the two eutectoid reactions as well as the measured solubility limits. Temperatures of 367°C and 536°C are calculated for the eutectoid reactions $\text{hP22} = \text{oS28} + \text{hP14}$ and $\text{hP22} = \text{hP14} + \text{oP28}$, respectively. These compare reasonably well with the values reported by [84] (374°C and 550°C, respectively) and by [249] (between 360 and 366°C, and between 550 and 552°C, respectively).

For the eutectoid temperature calculated at 367°C, both the data of Goldberg et al [84] and Amadori [249] were considered. For the eutectoid temperature calculated at 536°C, our DSC-TGA measurements for equilibrated chrome-glaserite (to which an excess of K_2CrO_4 was added subsequently) as well as the data of Goldberg et al [84] and Amadori [249] were taken into account.

The solubility limits for the two terminal solid solutions were estimated by Goldberg et al [84] using X-ray diffraction measurements of the lattice parameters. Our calculated maximum solubility of 1.4 mol% K_2CrO_4 (at 367°C) in oS28 is somewhat lower than the value of 4.0 mol% K_2CrO_4 reported by [84]. Our calculated maximum solubility of 7.0 mol% Na_2CrO_4 (at 536°C) in oP28 is identical to the value of Goldberg et al [84]. As shown in Figure 7.9, the upper phase boundary for the two-phase-region (hP22 + oP28) somewhat deviates from the available measurements. This is due in particular to our selected enthalpy change for the $\text{K}_2\text{CrO}_{4(\text{S1})} = \text{K}_2\text{CrO}_{4(\text{S2})}$ solid-solid transition, which was a weighted average of all available data from the literature [31].

Goldberg et al's DTA measurements [84] for Na_2CrO_4 -rich samples showed a very weak reversible peak at about 266°C, which was not observed for pure Na_2CrO_4 . This peak had its maximum intensity at 25 mol% K_2CrO_4 and then progressively disappeared around 50 mol% K_2CrO_4 [84]. Goldberg et al did not provide any interpretation for this thermal arrest. We concluded that it might be attributed to the formation of $\text{Na}_2\text{Cr}_2\text{O}_7$ or $\text{K}_2\text{Cr}_2\text{O}_7$ in the presence of small amounts of CrO_3 . Indeed, the reactions $\text{Na}_2\text{CrO}_4 + \text{CrO}_3 = \text{Na}_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{CrO}_4 + \text{CrO}_3 = \text{K}_2\text{Cr}_2\text{O}_7$ have very negative Gibbs energy changes at least up to the melting temperatures of the pure chromates. Also, the $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S1})} = \text{Na}_2\text{Cr}_2\text{O}_{7(\text{S2})}$ and $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S1})} = \text{K}_2\text{Cr}_2\text{O}_{7(\text{S2})}$ solid-solid transitions occur at 246°C and 258°C, respectively, which are relatively close to the value of 266°C [34].

The calculated ($\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) phase diagrams in the presence of 0.1 mol% CrO_3 are compared to the available measurements in Figures 7.11 and 7.12, respectively. Figure 7.11 includes as possible products the pure dichromates along with all dichromate-based solid solutions modeled in the present work (aP44, aP22 and $\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s.})$). The latter are described in Table 7.4 and will be discussed later. Figure 7.12 includes as possible products the pure dichromates, while the formation of all dichromate-based solid solutions is inhibited. It can be seen that the $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S1})} = \text{K}_2\text{Cr}_2\text{O}_{7(\text{S2})}$ solid-solid transition agrees closely with the thermal arrest observed around 266°C by Goldberg et al [84]. Thus, the latter might be due to trace amounts of CrO_3 in the Na_2CrO_4 and

K_2CrO_4 reagents used by these authors. However, it is unclear why the formation of the dichromate-based solid solutions would be impeded, thus favoring the formation of pure dichromates.

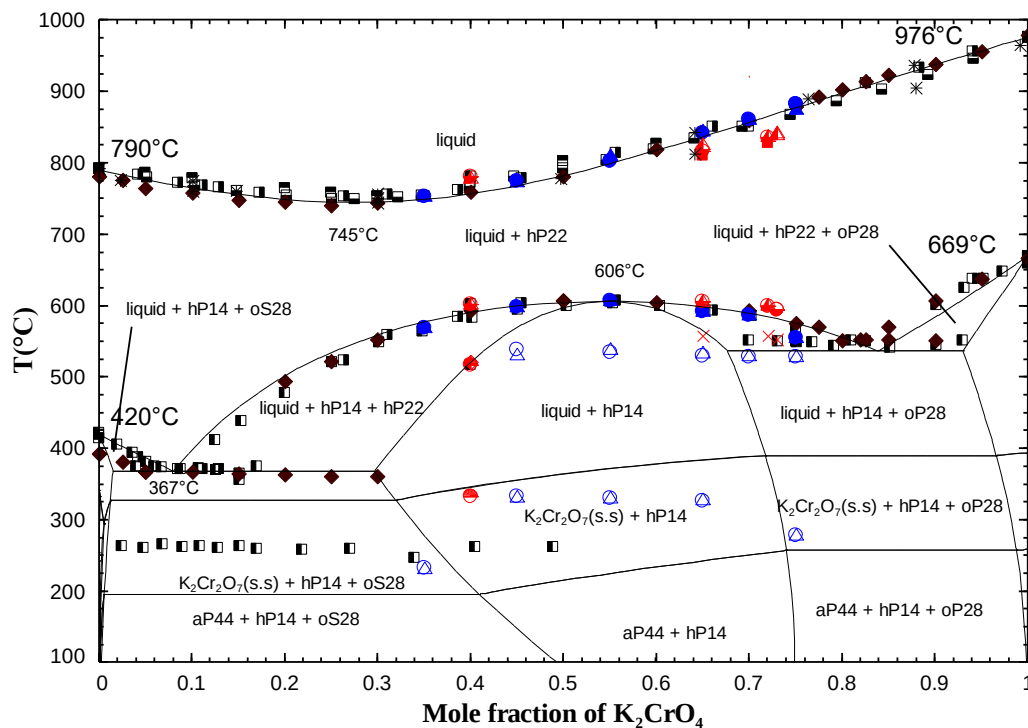


Figure 7.11 Calculated ($\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) phase diagram in presence of 0.1 mol% CrO_3 , with possible formation of the pure dichromates and all dichromate-based solid solutions (aP44, aP22 and $\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s})$)

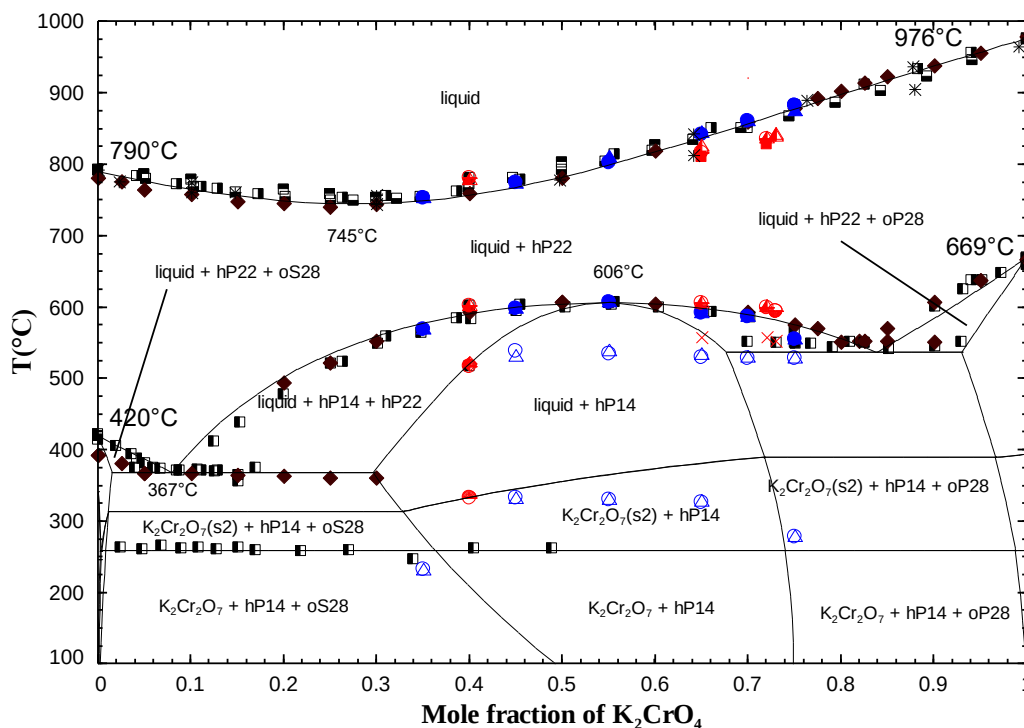


Figure 7.12 Calculated ($\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) phase diagram in presence of 0.1 mol% CrO_3 , with possible formation of the pure dichromates and with inhibited formation of all dichromate-based solid solutions (aP44, aP22 and $\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s})$)

7.6.8 The ($\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7$) system

The phase diagram has been measured by the method of cooling curves [132]. ($\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7$) is a simple eutectic system with no reported solid solutions or intermediate compounds. It was not possible to reproduce the data of Żemczużny [132] near pure KCl since its melting point reported by Żemczużny is about 20°C higher than the accepted value of 771°C selected in the present work [220]. Żemczużny [132] reported a eutectic at 72.5 mol% $\text{K}_2\text{Cr}_2\text{O}_7$ and 366°C . The calculated characteristics are 73.2 mol% $\text{K}_2\text{Cr}_2\text{O}_7$ and 364°C .

The binary liquid displays small negative deviations from ideality (Table 7.3). The calculated ($\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 7.13.

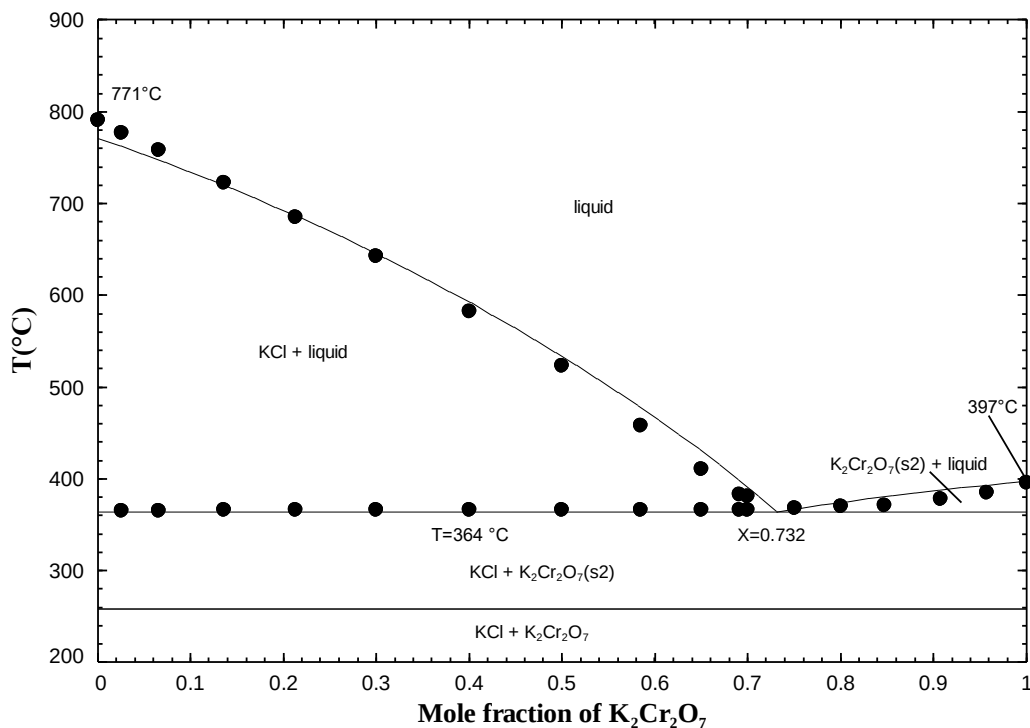


Figure 7.13 Calculated ($\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Żemczużny [132] (●)

7.6.9 The ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$) system

The phase diagram has been measured by the method of heating and cooling curves [131]. Groschuff reported a eutectic at 98.5 mol% $\text{K}_2\text{Cr}_2\text{O}_7$ and 393°C, which is very close to the melting point of pure potassium dichromate. The calculated characteristics of the eutectic are 96.1 mol% $\text{K}_2\text{Cr}_2\text{O}_7$ and 394°C. The binary liquid was assumed to be ideal (that is, $\Delta g_{\text{K}_2/(\text{CrO}_4)(\text{Cr}_2\text{O}_7)} = 0$). The calculated ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is shown along with the measurements in Figure 7.14.

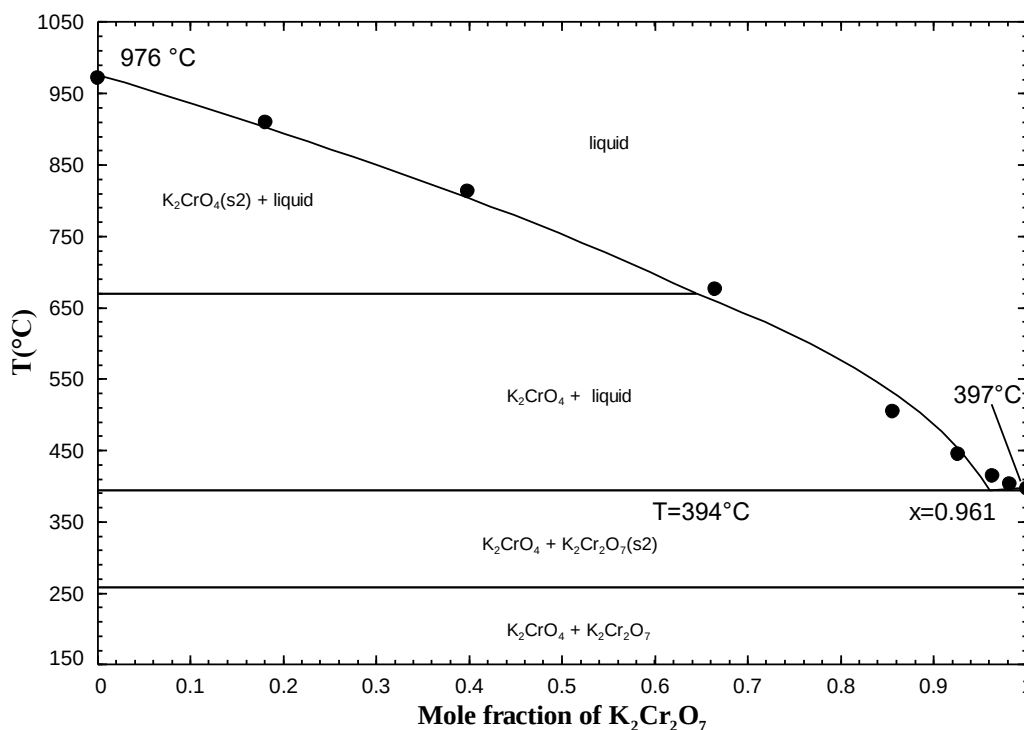
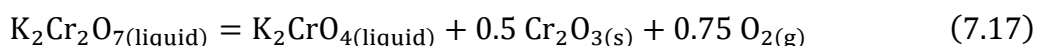


Figure 7.14 Calculated ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$).

Experimental data from Groschuff [131] (●)

Flood and Muan [254] measured the K_2CrO_4 content of ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{CrO}_4$) melts from 610 to 760°C, using a gravimetric method. These authors started with a weighted sample of $\text{K}_2\text{Cr}_2\text{O}_7$ saturated with Cr_2O_3 at a fixed partial pressure of $\text{O}_2(\text{g})$ of 1 atm or 0.21 atm (air). Under those conditions, the following equilibrium was reached :



The amount of $\text{O}_2(\text{g})$ expelled during adjustment to equilibrium was determined by weighing, after rapid cooling [254]. Starting from the K_2CrO_4 side of reaction (7.17) was unsuccessful; $\text{O}_2(\text{g})$ was consumed by the melt, but this process was extremely slow. By starting from the $\text{K}_2\text{Cr}_2\text{O}_7$ side of reaction (13), equilibrium was attained in two to six hours at $p(\text{O}_2) = 1 \text{ atm}$, but more time was required in air [254]. The calculated $\text{K}_2\text{Cr}_2\text{O}_7$ content (as a function of temperature) of ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{CrO}_4$) melts saturated with Cr_2O_3 and at a fixed partial pressure of $\text{O}_2(\text{g})$ of 1 atm or 0.21 atm is shown along with the measurements of Flood and Muan in Figure 7.15. The thermodynamic data for solid Cr_2O_3 were taken directly from the FToxid database in FactSage [42]. In Figure 7.15,

agreement is excellent between the calculations and the data. This confirms the validity of our assumption that the ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{CrO}_4$) liquid is ideal (which was based on the phase diagram data of Groschuff [131]).

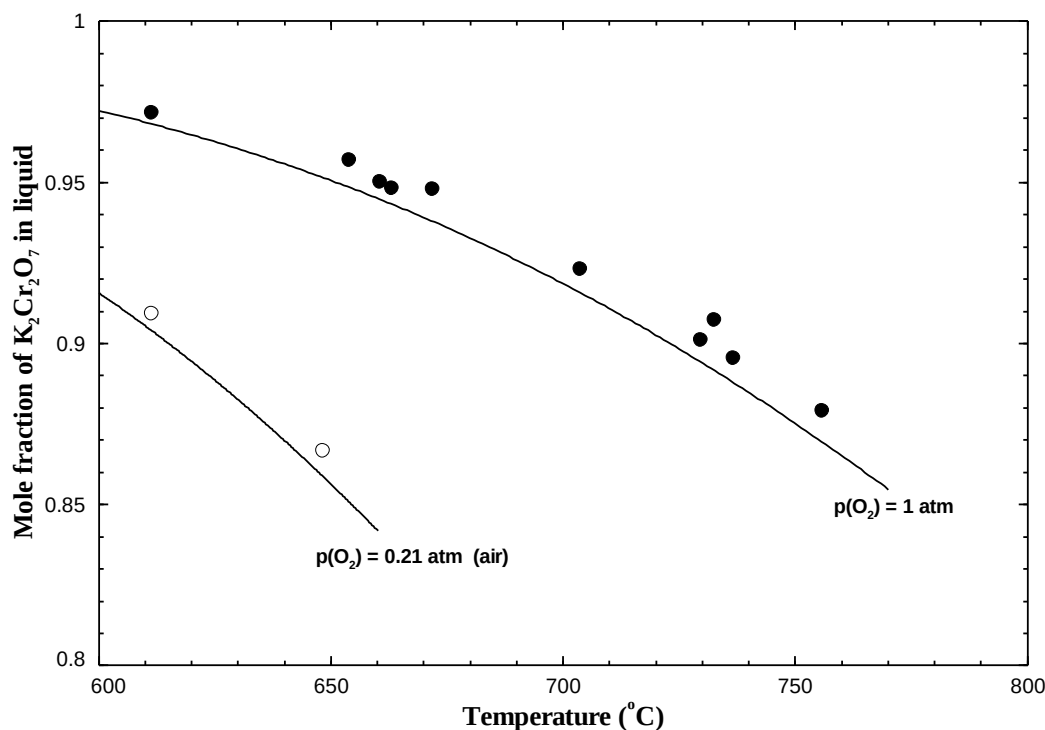


Figure 7.15 Calculated $\text{K}_2\text{Cr}_2\text{O}_7$ content of ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{CrO}_4$) melts saturated with Cr_2O_3 and at a fixed partial pressure of $\text{O}_2(\text{g})$ of 1 atm or 0.21 atm (air) Experimental data from Flood and Muan [254] (● : $p(\text{O}_2) = 1 \text{ atm}$, ○ : in air - $p(\text{O}_2) = 0.21 \text{ atm}$)

7.6.10 The ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7$) system

To our knowledge, this phase diagram has not been measured. Flood and Muan [254] measured the Na_2CrO_4 content of ($\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4$) melts from 400 to 550°C, using the same experimental protocol as described previously for the ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{CrO}_4$) system. The calculated $\text{Na}_2\text{Cr}_2\text{O}_7$ content (as a function of temperature) of ($\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4$) melts saturated with Cr_2O_3 and at a fixed partial pressure of $\text{O}_2(\text{g})$ of 1 atm is compared to the measurements of Flood and Muan in Figure 7.16. Different scenarios were considered. Scenario 1 corresponds to a ($\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4$) ideal liquid: the calculated $\text{Na}_2\text{Cr}_2\text{O}_7$ content is about 82.4 mol% at 405°C, which is significantly lower than the measured value of about 91.1 mol% [254]. Also, it decreases

much more rapidly with temperature than the data of Flood and Muan, and the liquid phase is calculated to disappear completely at about 448°C with the formation of $\text{Na}_2\text{CrO}_{4(\text{S}2)}$. This clearly disagrees with the results of those authors. The calculated $\text{Na}_2\text{Cr}_2\text{O}_7$ content of the melt depends on the Gibbs energy change for reaction (13) (in which K would be replaced with Na), which depends itself on the Gibbs energies of $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{liquid})}$, $\text{Na}_2\text{CrO}_{4(\text{liquid})}$, $\text{Cr}_2\text{O}_{3(\text{s})}$ and $\text{O}_{2(\text{g})}$. The Gibbs energy of liquid Na_2CrO_4 was evaluated by us from the literature [31], and is expected to be accurate. The thermodynamic data for $\text{O}_{2(\text{g})}$ are well-known; they were taken directly from the FactPS database in FactSage [42]. On the other hand, owing to the lack of data, some estimations were sometimes made for $\text{Na}_2\text{Cr}_2\text{O}_7$, and the selected thermodynamic data were therefore less accurate [34]. The thermodynamic data for $\text{Cr}_2\text{O}_{3(\text{s})}$ may be less accurate too : for instance, its $\Delta H_{298.15\text{ K}}^\circ$ value is -1,127,120 J/mol and -1,140,600 J/mol, respectively, in the FToxid and SGPS databases in FactSage [42]. There is a shift of about 13 kJ/mol between these two values. Calculations for $(\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{CrO}_4)$ melts were very satisfactory (see Figure 7.15), which suggests that the Gibbs energy of $\text{Cr}_2\text{O}_{3(\text{s})}$ is reasonably accurate between 610 and 760°C. However, it may be less accurate between 400 and 550°C. In Figure 7.16, scenario 2 corresponds to a $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4)$ ideal liquid, but the $\Delta H_{298.15\text{ K}}^\circ$ value for solid Cr_2O_3 is 6 kJ/mol higher than that for scenario 1. The calculated $\text{Na}_2\text{Cr}_2\text{O}_7$ content of about 89.7 mol% at 405°C is now close to the experimental value, and the liquid phase is calculated to be stable over the entire temperature range investigated by Flood and Muan.

The calculated $\text{Na}_2\text{Cr}_2\text{O}_7$ content of the binary melt also depends on the activities of $\text{Na}_2\text{Cr}_2\text{O}_7$ and Na_2CrO_4 in this melt. In scenario 3, the $\Delta H_{298.15\text{ K}}^\circ$ value for solid Cr_2O_3 is identical to that for scenario 2, but a parameter of $(-7,055 + 11 \cdot T)$ J/mol was introduced for the $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4)$ binary liquid. This model parameter permitted to introduce positive deviations from ideality and thus better reproduce the data of [254] up to about 450°C. From the three scenarios displayed in Figure 7.16, it can be concluded that arbitrary choices would need to be made in order to reproduce the measurements of Flood and Muan. Although the $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4)$ liquid may exhibit negative or positive deviations from ideality, it is expected to be relatively close to ideal owing to the similarity of the two anions. Finally, in the present work, it was assumed to be ideal (that is, $\Delta g_{\text{Na}_2/(\text{CrO}_4)(\text{Cr}_2\text{O}_7)} = 0$). The predicted phase diagram in air ($p(\text{O}_2) = 0.21\text{ atm}$) is shown in Figure

7.17. Measuring this phase diagram would permit to best calibrate the binary liquid.

Note that Flood and Muan [254] also measured the CrO_4 content of $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4)$ melts at 662°C over the entire range of Na/K molar ratios, using the same experimental protocol as described previously. Those data are not presented here since the same problem as for $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4)$ was encountered.

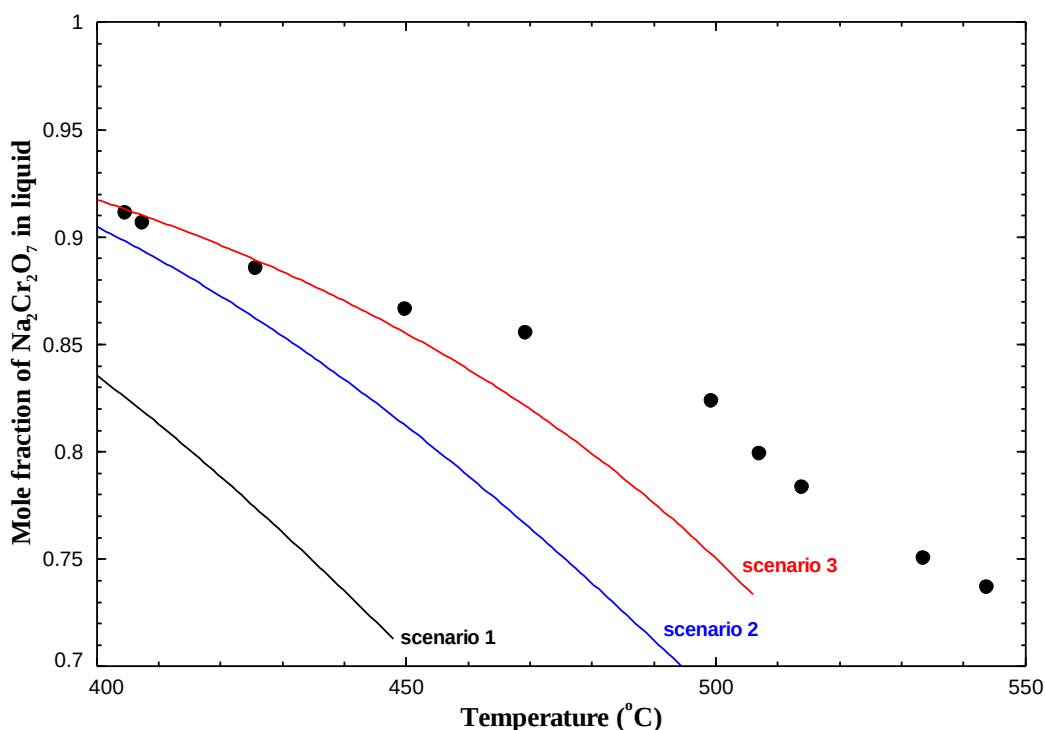


Figure 7.16 Calculated $\text{Na}_2\text{Cr}_2\text{O}_7$ content of $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4)$ melts saturated with Cr_2O_3 at $p(\text{O}_2) = 1$ atm. Scenario 1 : $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4)$ ideal liquid, and $\Delta H_{298.15\text{ K}}^\circ(\text{Cr}_2\text{O}_3(\text{s}))$ taken from the FToxid database; scenario 2 : $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4)$ ideal liquid, and $\Delta H_{298.15\text{ K}}^\circ(\text{Cr}_2\text{O}_3(\text{s}))$ is 6 kJ/mol higher than that from the FToxid database; scenario 3 : parameter of $(-7,055 + 11 \cdot T)$ J/mol for the $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{CrO}_4)$ liquid, and $\Delta H_{298.15\text{ K}}^\circ(\text{Cr}_2\text{O}_3(\text{s}))$ is 6 kJ/mol higher than that from the FToxid database. Experimental data from Flood and Muan [254] (●)

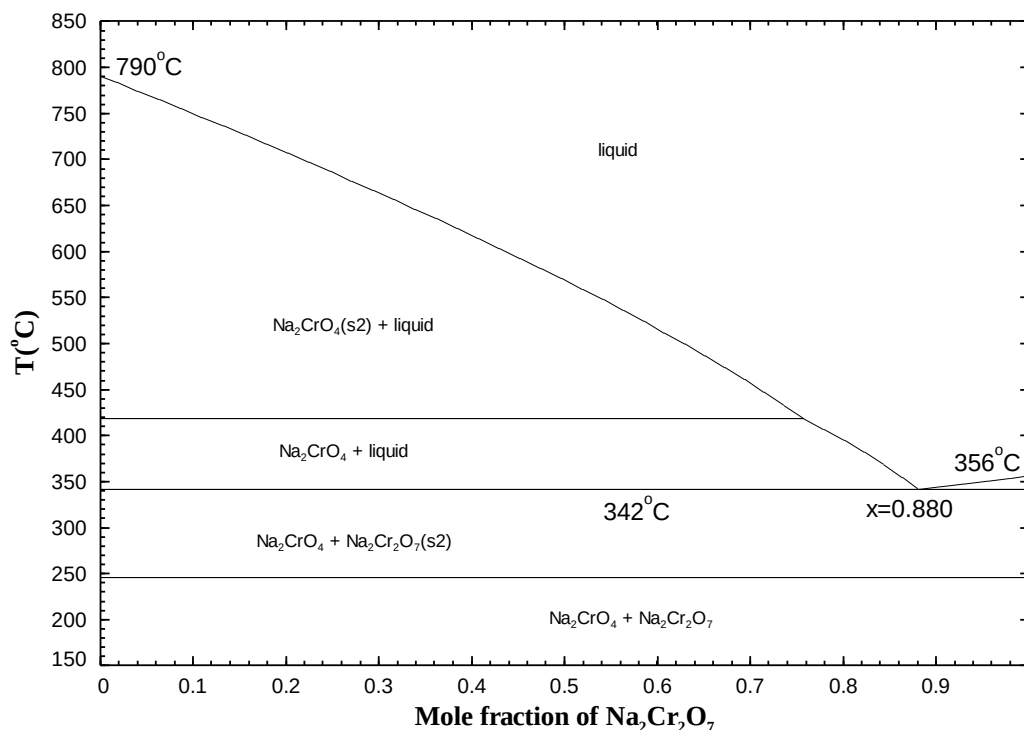


Figure 7.17 Calculated (predicted) ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21$ atm), for an ideal liquid

7.6.11 The ($\text{Na}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Cr}_2\text{O}_7$) system

The phase diagram has been measured by thermal analysis and visual observation for the determination of the liquidus curves [201], and by the method of heating and cooling curves [255]. Lehrman et al [201] reported the presence of a eutectic plateau from 22.9 to 84.7 mol% $\text{K}_2\text{Cr}_2\text{O}_7$ at a temperature of about 303 to 306°C, based on thermal analysis. Palkin and Bokhovkin [255] reported a eutectic at 42.5 mol% $\text{K}_2\text{Cr}_2\text{O}_7$ and 300°C. The calculated characteristics of the eutectic are 44.7 mol% $\text{K}_2\text{Cr}_2\text{O}_7$ and 298°C. The data of [201] and [255] are somewhat different but were both considered in our model.

As shown in Table 7.1, the high-temperature allotropes $\text{Na}_2\text{Cr}_2\text{O}_7(\text{s}_2)$ and $\text{K}_2\text{Cr}_2\text{O}_7(\text{s}_2)$ do not have the same crystal structure. Therefore, two high-temperature terminal solid solutions (aP22 and $\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s})$) were introduced. The calculated solid solubility limits at the eutectic temperature of 298°C are 26.5 and 82.4 mol% $\text{K}_2\text{Cr}_2\text{O}_7$, respectively. These agree reasonably well with the

experimental values of 25.0 and 79.0 mol% $\text{K}_2\text{Cr}_2\text{O}_7$ reported by Palkin and Bokhovkin [255].

As seen in Table 7.1, the low-temperature allotropes $\text{Na}_2\text{Cr}_2\text{O}_7(\text{s}_1)$ and $\text{K}_2\text{Cr}_2\text{O}_7(\text{s}_1)$ have the same crystal structure and space group $\text{P}\bar{1}$. Therefore, a low-temperature solid solution (aP44) was introduced over the entire composition range. A very positive regular parameter of +20,000.0 J/mol was arbitrarily introduced in this solid solution in order to reduce its calculated extent and permit the reproduction of the high-temperature data of [201] and [255] with the two high-temperature terminal solid solutions. A miscibility gap (related to aP44) was calculated at low temperatures.

The binary liquid was assumed to be ideal (that is, $\Delta g_{\text{NaK/Cr}_2\text{O}_7} = 0$) owing to the similarity of the cationic radii [214]. The calculated ($\text{Na}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Cr}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 7.18.

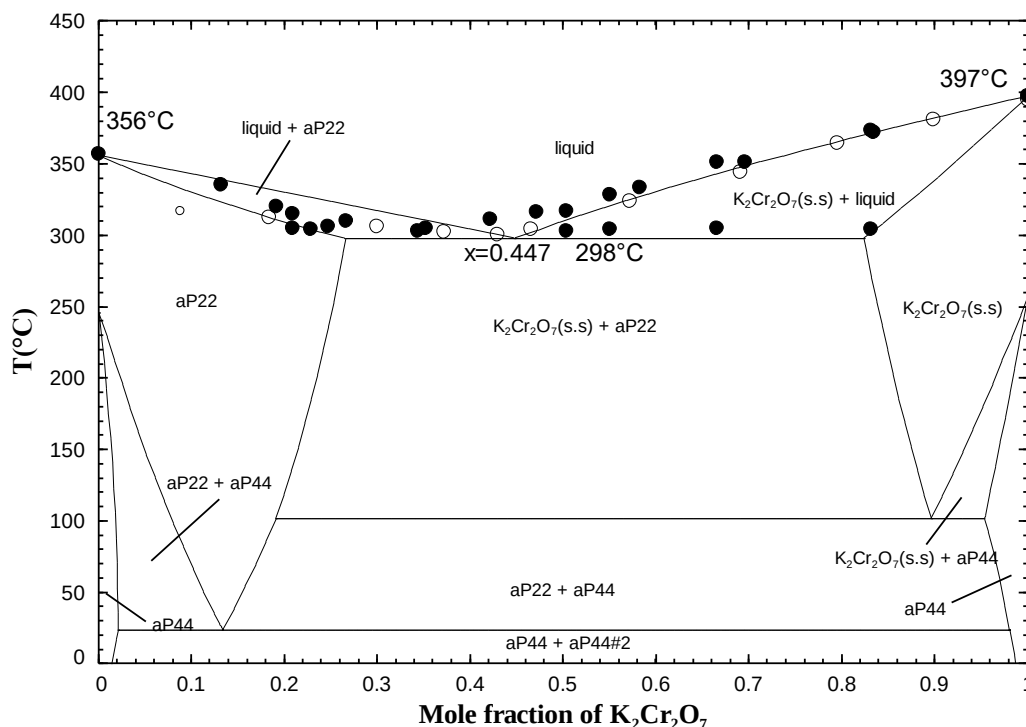


Figure 7.18 Calculated ($\text{Na}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Cr}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Lehrman et al [201] (●) and Palkin and Bokhovkin [255] (○, extracted from [256])

7.7 Chromate-based common-cation ternary sub-systems

7.7.1 The ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$) system

Bergman and Sanzharov [257] studied the liquidus surface of the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$) system using the visual-polythermal method. Eight isoplethal sections were measured, but no data were reported. Only a smoothed liquidus projection was provided by the authors. Thus, the intersections between the eight isoplethal sections and the drawn isotherms were extracted graphically. Figure 7.19 displays the calculated liquidus projection along with the data points extracted graphically.

The ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$) binary sub-system was modelled previously [40], and the corresponding model parameters were used directly in the present work. No ternary excess parameter was included for the liquid phase. Overall, agreement was satisfactory owing to the uncertainty related to the graphical extraction of the intersection points from a smoothed liquidus projection. As seen in Figure 7.19, the measured composition of the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$) binary mixture at 850°C disagrees with the calculated composition, which was based on experimental data from the literature [40].

Bergman and Sanzharov [257] reported a ternary eutectic reaction at 648°C and liquid composition of (46 mol% Na_2CO_3 + 3 mol% Na_2SO_4 + 51 mol% Na_2CrO_4). The hexagonal solid solution hP22 is calculated to precipitate from the liquid phase over the entire composition range. Close to the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4$) binary sub-system, there is a calculated univariant line corresponding to a solid-solid miscibility gap.

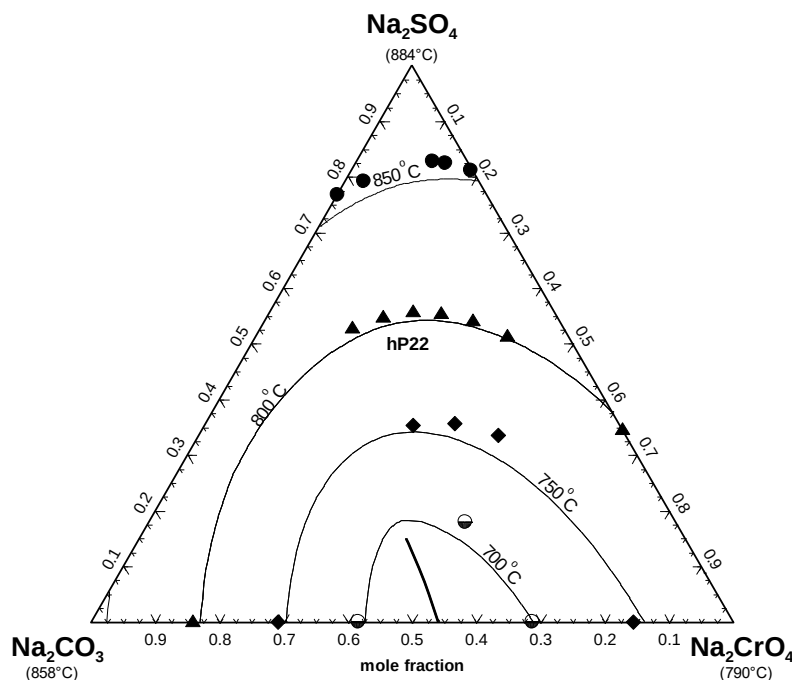


Figure 7.19 Calculated liquidus projection of the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$) system.

Experimental data for isotherms (● : 850°C, ▲ : 800°C, ◆ : 750°C, ⊖ : 700°C) were extracted graphically from the smoothed liquidus projection of Bergman and Sanzharov [257]

7.7.2 The ($\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system

Sanzharov and Bergman [245] investigated the liquidus surface of the ($\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system by the visual-polythermal method. Ten isoplethal sections were studied but measurements were reported only for two of them. The calculated liquidus projection is shown in Figure 7.20, and the two calculated isoplethal sections are compared to the available data points in Figures 7.21 and 7.22. The ($\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4$) binary sub-system was modelled previously [40], and the corresponding model parameters were used directly in the present work. A small ternary excess parameter was included for the liquid phase (Table 7.3). Measurements in Figure 7.21 agree better with the calculated solidus, whereas data in Figure 7.22 agree better with the calculated liquidus. In Figures 7.21 and 7.22, predictions made solely from the optimized model parameters for the three common-cation binary sub-systems are also displayed as red lines.

Sanzharov and Bergman [245] reported a ternary eutectic reaction at 786°C and liquid composition of (62 mol% K_2CO_3 + 1.5 mol% K_2SO_4 + 36.5 mol% K_2CrO_4). This is not possible since, as seen

in Figure 7.20, the hexagonal solid solution hP22 precipitates from the liquid phase over the entire composition range. Therefore, there are no calculated ternary invariant points.

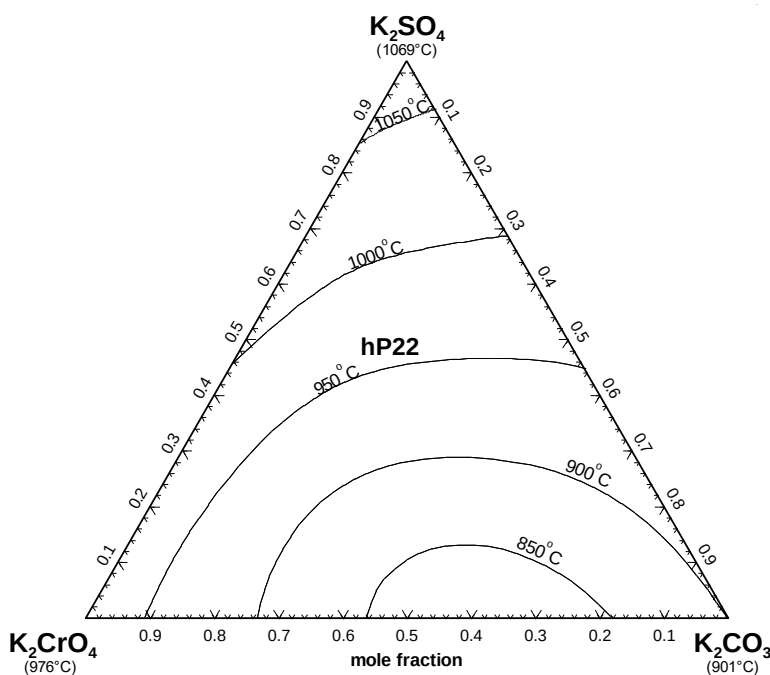


Figure 7.20 Calculated liquidus projection of the ($\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system

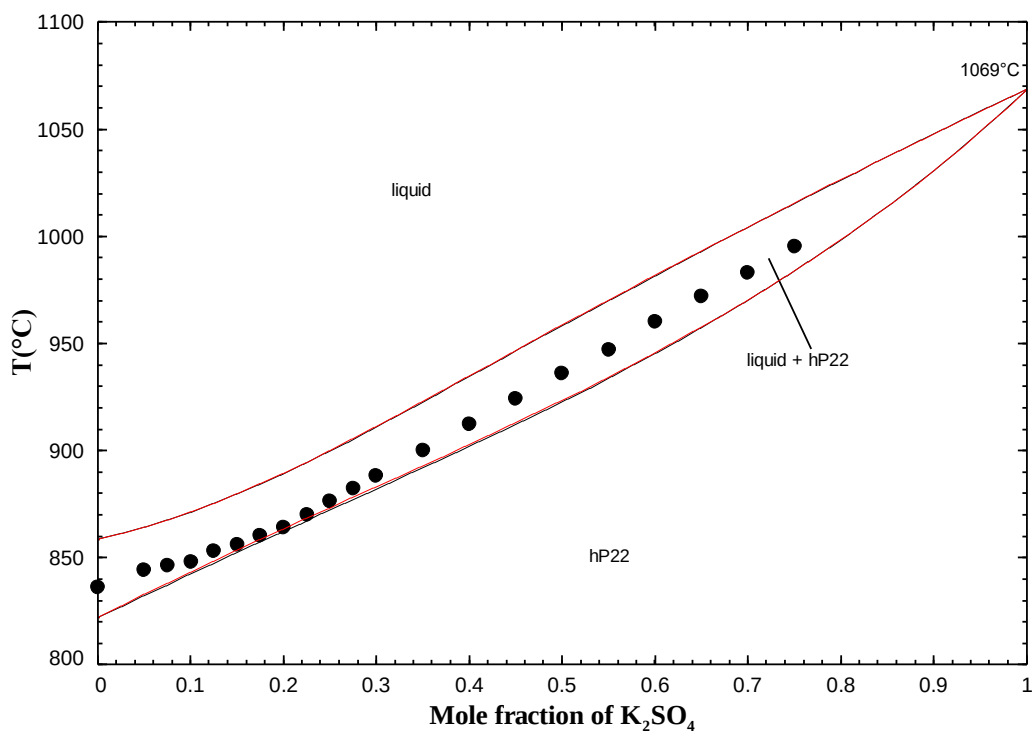


Figure 7.21 Calculated isoplethal section in the $(\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4)$ system $((\text{K}_2\text{CO}_3)_{0.85}(\text{K}_2\text{CrO}_4)_{0.15}-\text{K}_2\text{SO}_4)$. Black lines : final calculations (with one ternary excess parameter); red lines : predictions (without any ternary excess parameter). Experimental data from [245] (●)

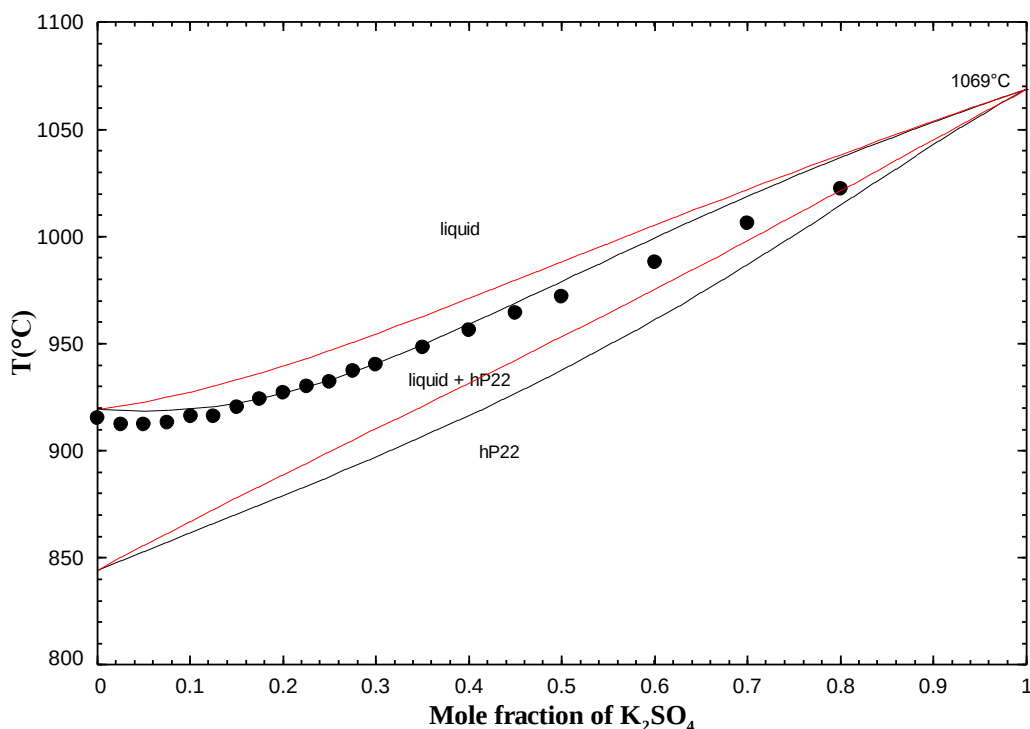


Figure 7.22 Calculated isoplethal section in the $(\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4)$ system $((\text{K}_2\text{CO}_3)_{0.20}(\text{K}_2\text{CrO}_4)_{0.80}-\text{K}_2\text{SO}_4)$. Black lines : final calculations (with one ternary excess parameter); red lines : predictions (without any ternary excess parameter). Experimental data from [245] (●)

7.7.3 The $(\text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ system

To our knowledge, no ternary phase diagram data are available for the $(\text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ system. The calculated liquidus projection is displayed in Figure 7.23. No ternary excess parameter was included for the liquid phase. That is, the liquidus projection was predicted solely from the optimized model parameters for the three common-cation binary sub-systems. The $(\text{KCl} + \text{K}_2\text{CO}_3)$ binary sub-system was modelled previously [41], and the corresponding model parameters were used directly in this work.

The ternary eutectic reaction $\text{liquid} = \text{KCl}_{(\text{s})} + \text{hP22} + \text{oP28}$ is predicted at 593°C and liquid composition of (54.7 mol% KCl + 27.8 mol% K_2CO_3 + 17.5 mol% K_2CrO_4), and the ternary quasi-peritectic reaction $\text{liquid} + \text{hP22} = \text{hP22} + \text{oP28}$ is predicted at 630°C and liquid composition of (46.4 mol% KCl + 31.5 mol% K_2CO_3 + 22.1 mol% K_2CrO_4).

In this study, DSC-TGA measurements were conducted for the ternary composition (55.0 mol% KCl + 28.0 mol% K_2CO_3 + 17.0 mol% K_2CrO_4) from 200 to 645°C . The corresponding DSC thermogram is shown in Figure 7.24. There is a single thermal arrest around 596°C (the average value of the temperatures measured during the second and third heating runs). This experimental ternary eutectic is, therefore, very well predicted by our model. This is an important feature since the formation of a liquid phase at low temperatures (such as ternary eutectics) may lead to catastrophic corrosion.

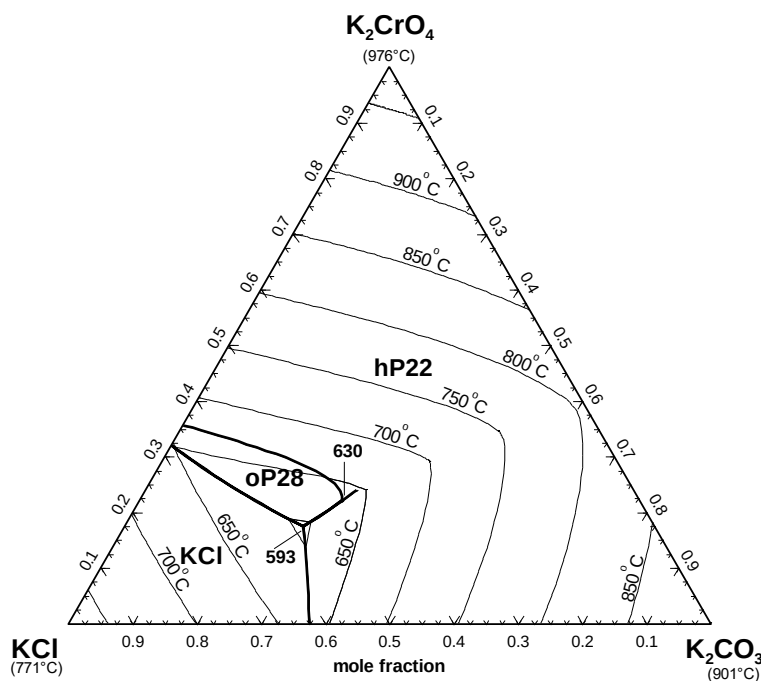


Figure 7.23 Calculated liquidus projection of the ($\text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4$) system

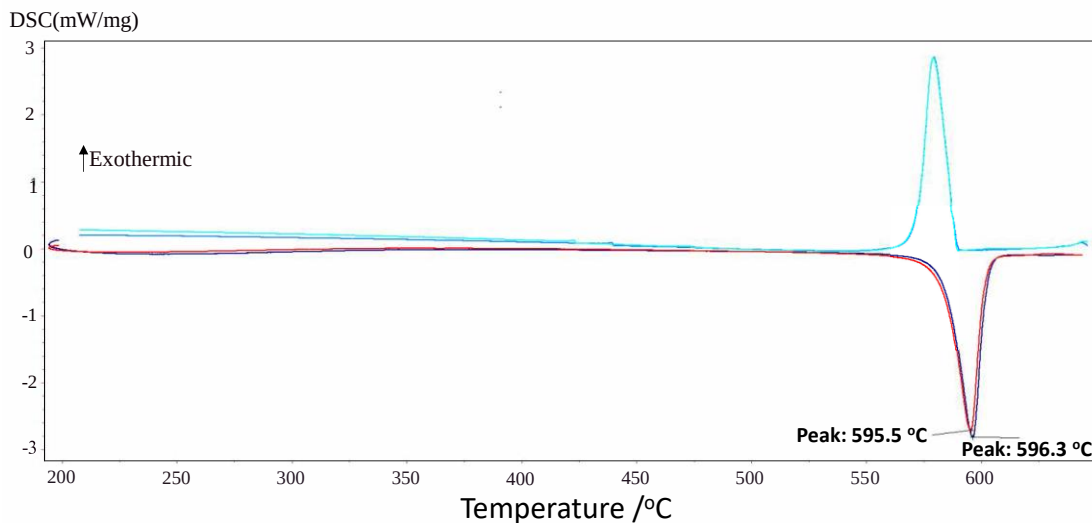


Figure 7.24 DSC thermogram for the ternary mixture (55.0 mol% KCl + 28.0 mol% K₂CO₃ + 17.0 mol% K₂CrO₄) (2nd and 3rd heating/cooling cycles only)

7.8 Chromate-based ternary reciprocal sub-systems

7.8.1 The (Na₂SO₄ + K₂SO₄ + Na₂CrO₄ + K₂CrO₄) system

The calculated liquidus projection of the (Na₂SO₄ + K₂SO₄ + Na₂CrO₄ + K₂CrO₄) ternary reciprocal system is shown in Figure 7.25. In the reciprocal square in this figure, the four apices correspond to the pure salts : Na₂SO₄, K₂SO₄, Na₂CrO₄ and K₂CrO₄. In order for tie-lines to be straight lines, the compositions are expressed in terms of cationic and anionic equivalent fractions. In Figure 7.25, the X-axis corresponds to the cationic molar ratio $n_K/(n_{Na} + n_K)$, and the Y-axis corresponds to the anionic molar ratio $n_{CrO_4}/(n_{SO_4} + n_{CrO_4})$. No ternary reciprocal parameter was included for the liquid phase. That is, calculations in the (Na₂SO₄ + K₂SO₄ + Na₂CrO₄ + K₂CrO₄) system were solely predicted from the optimized model parameters for the four common-ion binary sub-systems. The (Na₂SO₄ + K₂SO₄) binary sub-system was modelled previously [39], and the corresponding model parameters were used directly in the present work. As seen in Figure 7.25, the hexagonal solid solution hP22 precipitates from the liquid phase over the entire composition range.

Using the method of cooling curves, Flach [112] measured the section (K₃Na(SO₄)₂ + K₃Na(CrO₄)₂), extending from the sulfur-glaserite to the chrome-glaserite which were both

modeled with the hP14 non-stoichiometric compound. The calculated section is shown along with the measurements in Figure 7.26. The agreement is excellent. Three different solid solutions (hP22, hP14 and oP28) can precipitate. Note that several calculated thermal arrests (in particular, the solidus of the hexagonal solid solution hP22) were not observed experimentally by Flach [112].

Bergman and Sanzharov [258] measured the ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) diagonal section using the visual-polythermal method, and reported a marked minimum at 32.5 mol% K_2CrO_4 and 780°C. No measurements were reported, and therefore the data points were extracted graphically from the smoothed liquidus projection provided by the authors for the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system. The calculated ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) phase diagram is shown in Figure 7.27 along with the data points extracted graphically. The agreement is very satisfactory.

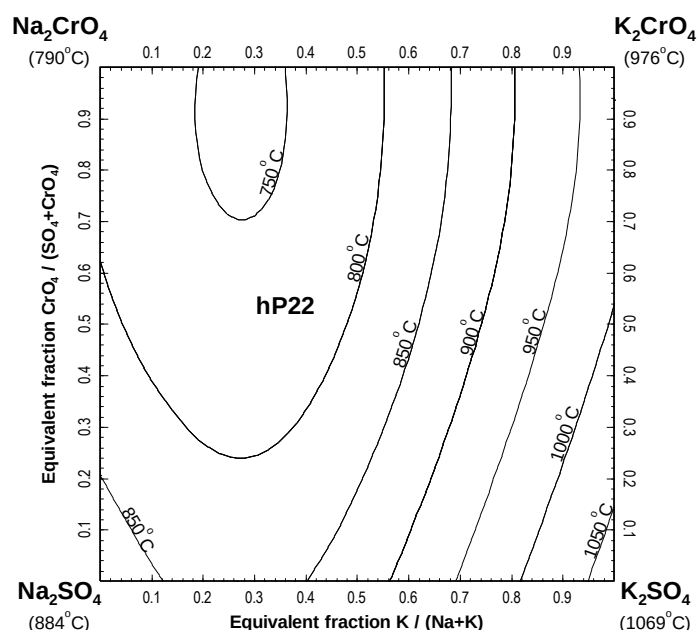


Figure 7.25 Calculated liquidus projection of the ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) system

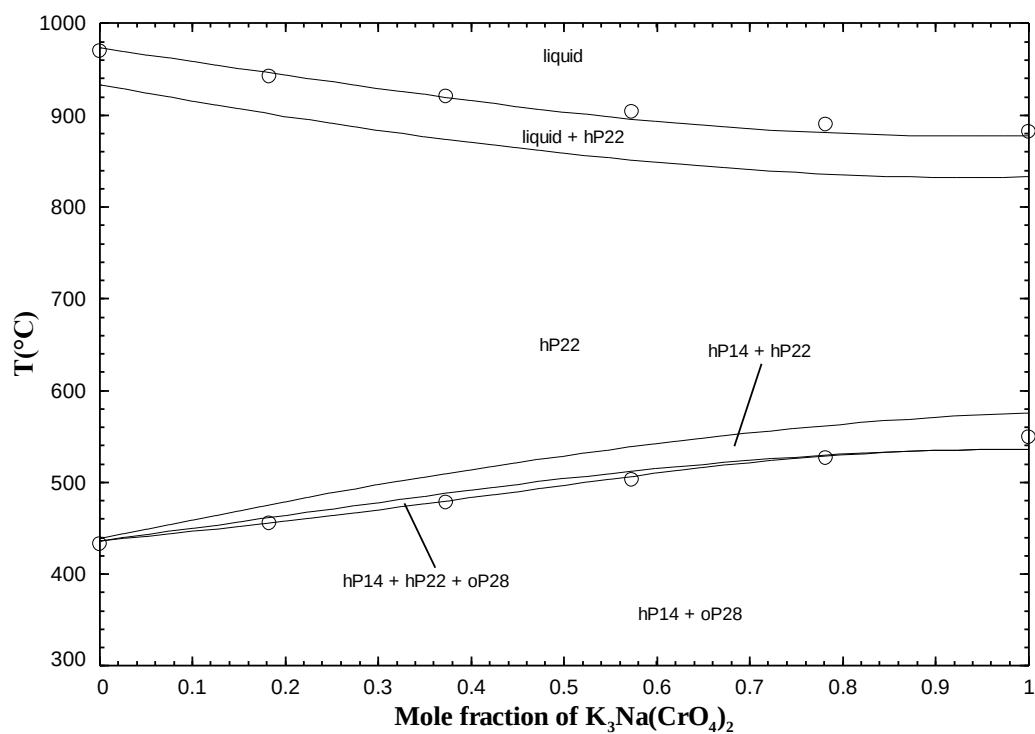


Figure 7.26 Calculated ($\text{K}_3\text{Na}(\text{SO}_4)_2 + \text{K}_3\text{Na}(\text{CrO}_4)_2$) section in the ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) system. Experimental data from Flach [112] (○)

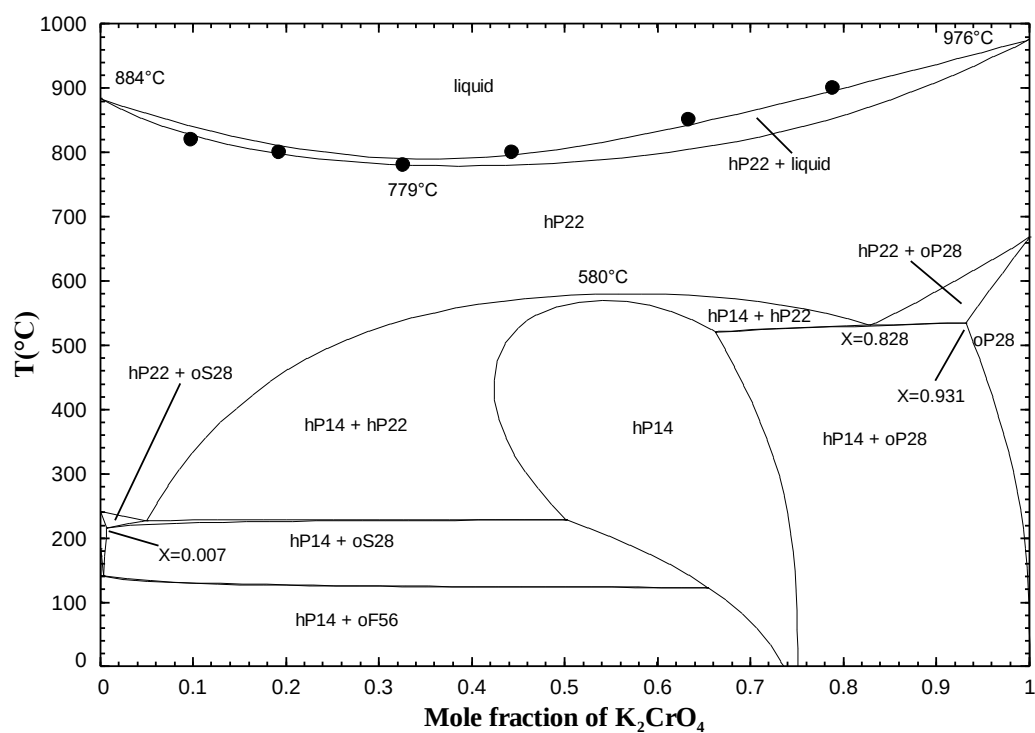


Figure 7.27 Calculated ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) section in the ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) system. Experimental data (●) were extracted graphically from the smoothed liquidus projection of Bergman and Sanzharov [258] for the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system

7.8.2 The ($\text{NaCl} + \text{KCl} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) system

The calculated liquidus projection of the ($\text{NaCl} + \text{KCl} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) ternary reciprocal system is displayed in Figure 7.28. No ternary reciprocal parameter was included for the liquid phase. The ($\text{NaCl} + \text{KCl}$) binary sub-system was modelled previously [220], and the corresponding model parameters were used directly in the present work. Using the visual-polythermal method, Bergman and Trunin [259] investigated fifteen isoplethal sections for their construction of the liquidus surface of this system. Unfortunately, these data points have limited accuracy since only their measured liquidus temperatures were reported and their ternary compositions had to be extracted graphically from a smoothed liquidus projection provided by the authors. Each isoplethal section investigated by Bergman and Trunin [259] consisted of a common-cation binary mixture to which was added a pure salt or another common-cation binary mixture.

For the sake of comparison between the calculations and the measurements, there were enough ternary compositions studied for only six of the fifteen isoplethal sections. For each of those six isoplethal sections, the composition of the binary mixture was assessed as accurately as possible by considering simultaneously the intersection point with the relevant side of the reciprocal square along with the graphically extracted ternary compositions investigated by Bergman and Trunin [259].

As an example, two calculated isoplethal sections are compared to the measurements in Figures 7.29 and 7.30. The remaining four isoplethal sections are given in the Supplementary Information (see Figures C2 to C5). Overall, the agreement was satisfactory owing to the uncertainty related to the graphical extraction of the compositions from a smoothed liquidus projection.

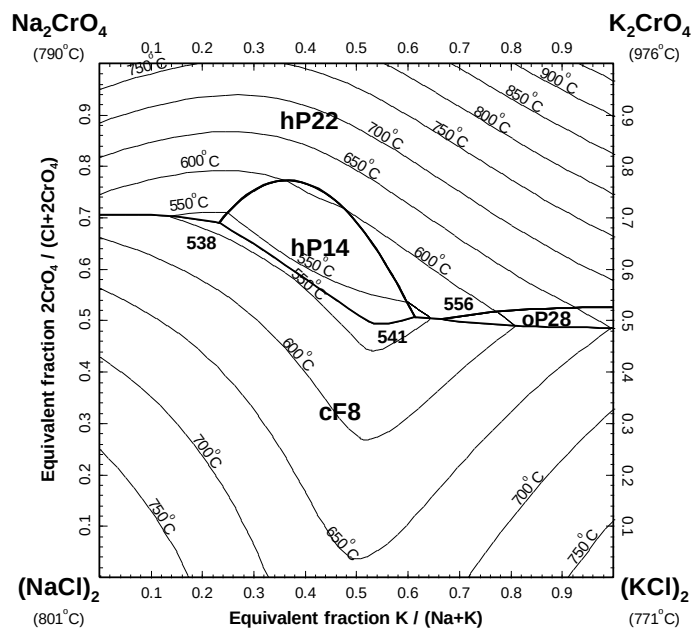


Figure 7.28 Calculated liquidus projection of the (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) system

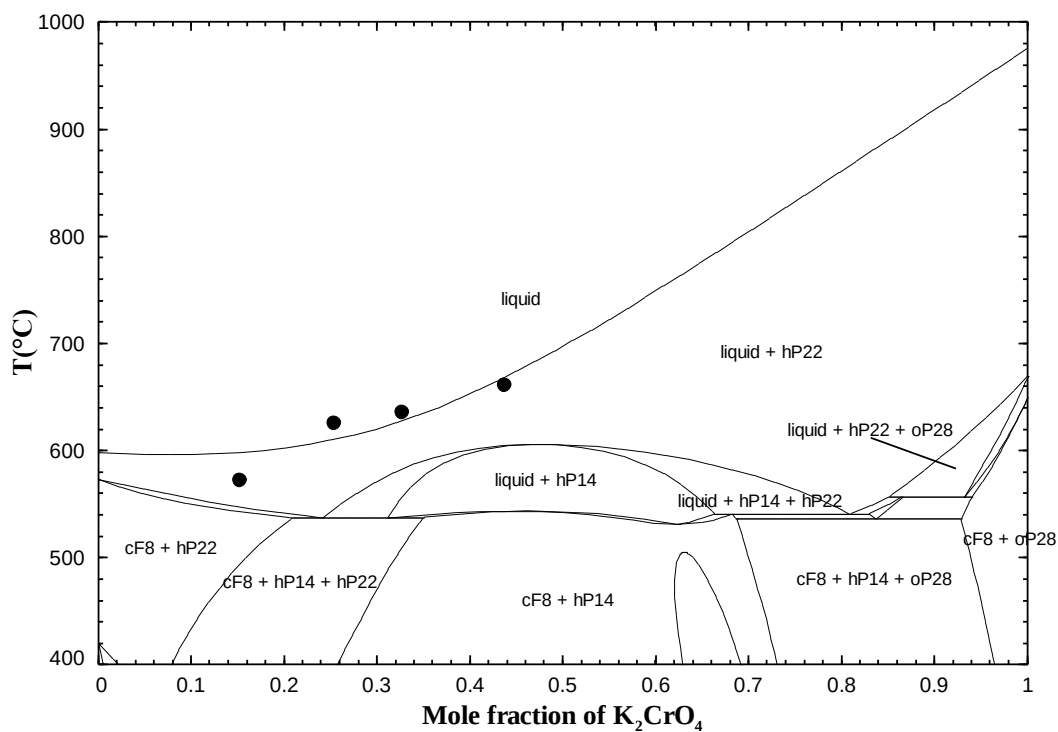


Figure 7.29 Calculated isoplethal section in the (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) system ((Na₂CrO₄)_{0.743}(Na₂Cl₂)_{0.257}-K₂CrO₄, section III). Experimental data extracted graphically from the liquidus projection of Bergman and Trunin [259] (●)

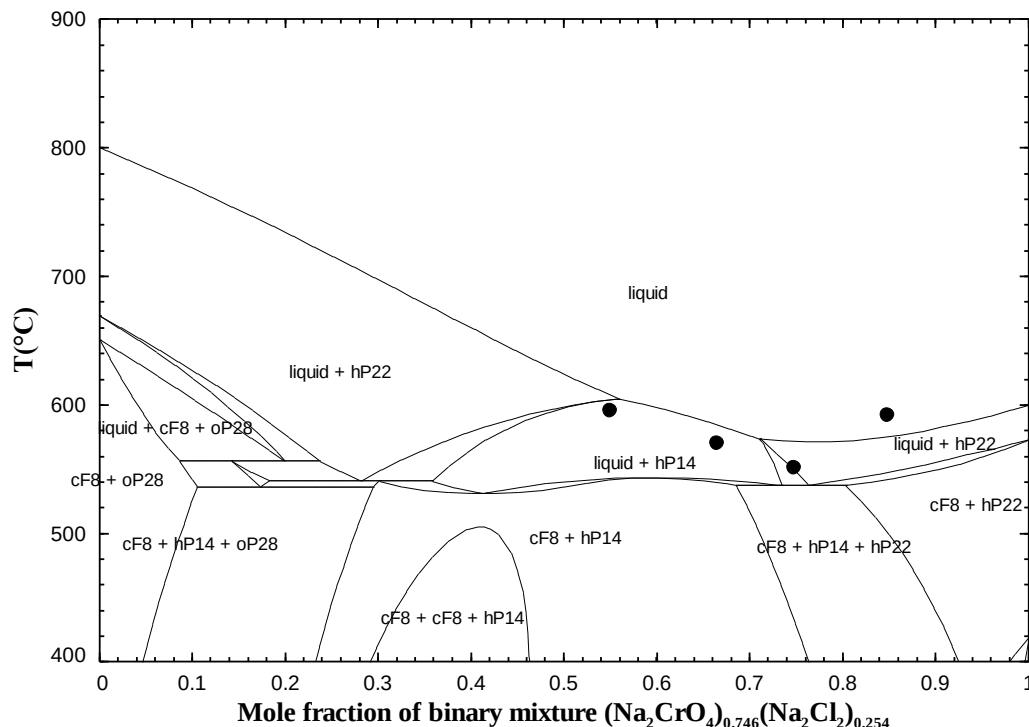


Figure 7.30 Calculated isoplethal section in the $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4)$ system $((\text{K}_2\text{CrO}_4)_{0.746}(\text{K}_2\text{Cl}_2)_{0.254} - (\text{Na}_2\text{CrO}_4)_{0.746}(\text{Na}_2\text{Cl}_2)_{0.254}$, section XII). Experimental data extracted graphically from the liquidus projection of Bergman and Trunin [259] (●)

7.8.3 The $(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4)$ system

Bergman and Sanzharov [258] measured the $(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ diagonal section using the visual-polythermal method, and reported a eutectic point at 37.5 mol% K_2CrO_4 and 635°C. Three small ternary reciprocal parameters were included in the liquid phase in order to best reproduce those data (see Table 7.3). Again, no measurements were reported, and therefore the data points were extracted graphically from the smoothed liquidus projection provided by the authors for the $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4)$ system. The calculated liquidus projection of the $(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4)$ ternary reciprocal system is displayed in Figure 7.31. The hexagonal hP22 solid solution is calculated to precipitate over the entire composition range. The calculated univariant line does not reach the $(\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ binary sub-system since this system exhibits a minimum (see Figure 7.6). The calculated $(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ phase diagram in air ($p(\text{O}_2) = 0.21$

atm) is shown in Figure 7.32 along with the data points extracted graphically. (The calculated isobar at 1 atm is also displayed.)

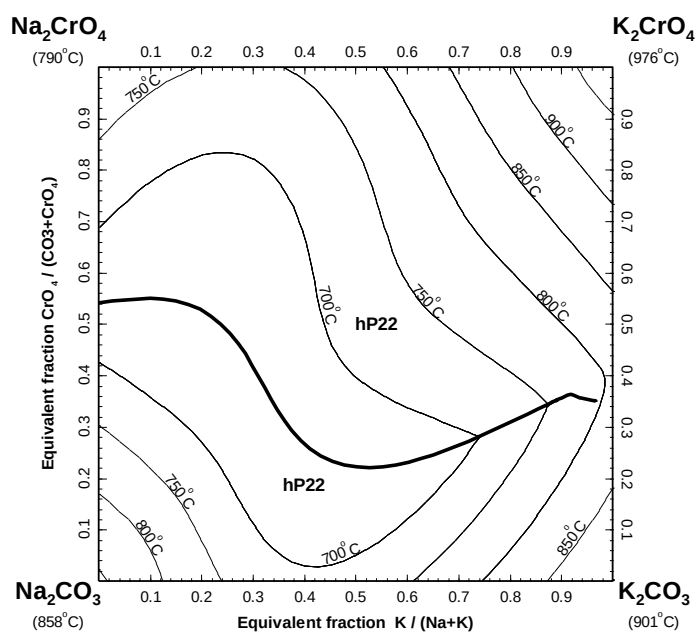


Figure 7.31 Calculated liquidus projection of the ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) system

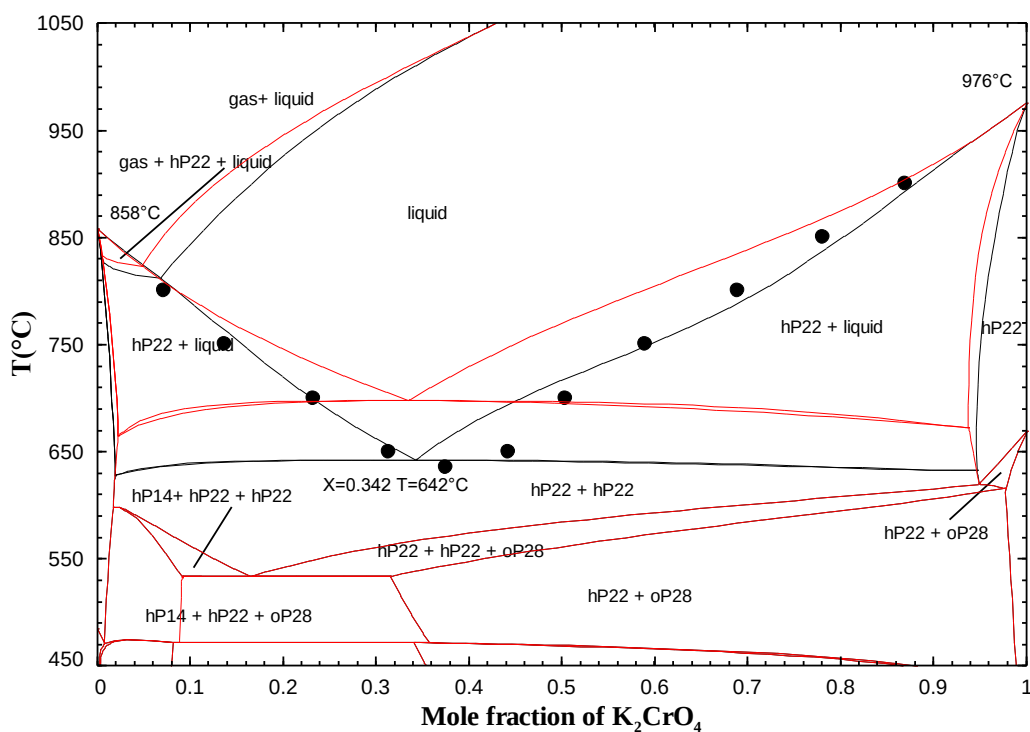


Figure 7.32 Calculated ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CrO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Black lines: final calculations (with three ternary reciprocal parameters); red lines : predictions (without any ternary reciprocal parameter). Experimental data (●) were extracted graphically from the smoothed liquidus projection of Bergman and Sanzharov [258] for the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system

7.9 The ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) quaternary reciprocal sub-system

Using the visual-polythermal method, Bergman and Sanzharov [258] investigated the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system and measured nine isoplethal sections. Again, no measurements were reported, and only a smoothed liquidus projection was provided for this system. Therefore, the intersections between the nine isoplethal sections and the drawn isotherms were extracted graphically. The calculated (predicted) liquidus projection of the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system is compared to the extracted data points in Figure 7.33. The ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$) ternary reciprocal sub-system was modelled previously [40], and the corresponding model parameters were used directly in the present work. Note that no higher-order model parameters than ternary reciprocal parameters are available in the MQMQA. Sometimes, significant shifts were observed between the measured and calculated isotherms. This may be partly due to the limited accuracy of the data points extracted graphically. Also, the measured compositions of the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$) common-cation binary mixtures at 800 and 850°C disagree substantially with the calculated compositions, which were based on experimental data from the literature [40].

Bergman and Sanzharov [258] reported a liquidus temperature of 632°C for the composition (54 mol% $\text{Na}_2\text{CO}_3 + 13 \text{ mol\% Na}_2\text{SO}_4 + 33 \text{ mol\% K}_2\text{CrO}_4$) [258]. The calculated liquidus temperature is 647°C.

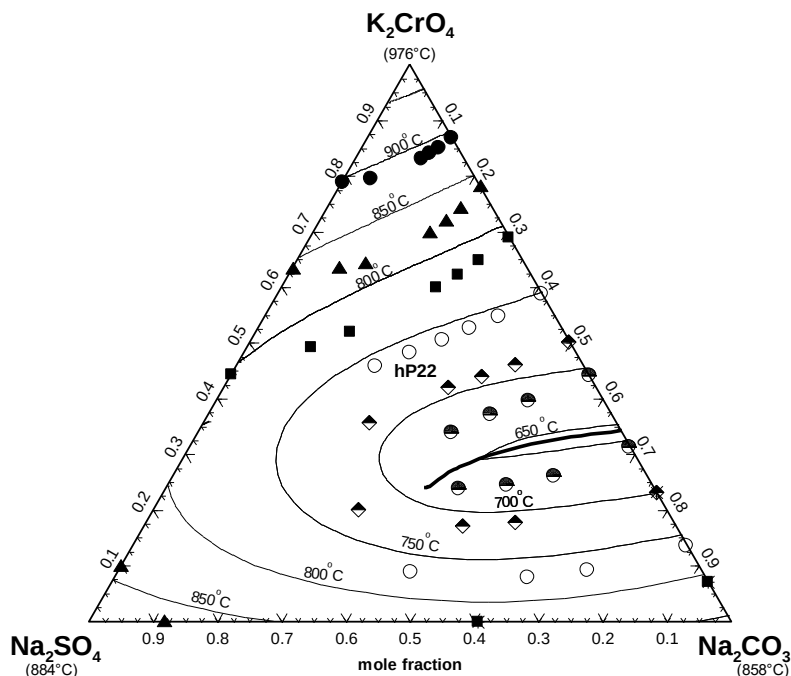


Figure 7.33 Calculated liquidus projection of the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) system. Experimental data for isotherms (● : 900°C, ▲ : 850°C, ■ : 800°C, ○ : 750°C, ◆ : 700°C, and ◐ : 650°C) were extracted graphically from the smoothed liquidus projection of Bergman and Sanzharov [258]

7.10 Multicomponent system ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{O}$) (diluted in free oxides)

For the liquid phase of the 14-component system (diluted in free oxides), the model described in section 3 was used. Phase diagram data were somewhat limited for Na_2CrO_4 - and K_2CrO_4 -containing ternary common-cation sub-systems, ternary reciprocal sub-systems (i.e. systems with Na, K, and two anions) and higher-order sub-systems. Such data were available for the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$), ($\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$), ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$), ($\text{NaCl} + \text{KCl} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$), and ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) systems. One small ternary excess parameter and three small ternary reciprocal parameters were required for the ($\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) and ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) systems, respectively, while satisfactory predictions were obtained in all remaining systems. For all ternary and ternary

reciprocal sub-systems evaluated in the present work and previously [39-41] no, or only small, ternary or ternary reciprocal excess parameters were required to reproduce the available data. The assumption 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 result in accurate predictions of the 14-component liquid phase (diluted in free oxides).

Several multicomponent solid solutions (hP22, oS28, oP28, hP14, oF56, and aP22) were modeled in this work and previously [39-41] using the model described in section 3 for hP22 and the model described in section 4 for all other solid solutions. Experimental phase equilibria involving hP22, hP14 and oP28 were satisfactorily reproduced in the ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) and ($\text{NaCl} + \text{KCl} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) ternary reciprocal sub-systems without the introduction of any additional parameters in the models for those solid solutions. Therefore, our thermodynamic model is expected to result in accurate predictions of phase equilibria in the multicomponent system.

7.11 Conclusions

In this paper and previous articles [39-41], a complete critical evaluation of all available phase diagram and thermodynamic data for all condensed phases of the ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{O}$) system has been made, and optimized model parameters have been found. The oxides are present in dilute amounts in the liquid phase since reactions of the type $2 \text{A}_2\text{CrO}_4 = \text{A}_2\text{Cr}_2\text{O}_7 + \text{A}_2\text{O}$ (where $\text{A} = \text{Na}, \text{K}$) are very limited up to above the liquidus temperatures [34]. All chromate-based and dichromate-based sub-systems for which data (mainly phase equilibria) were available have been considered. In addition, owing to the lack of data, DSC-TGA experiments were conducted for several compositions in the common-ion binary sub-systems ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4$), ($\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4$) and ($\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$). In ($\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4$), a miscibility gap related to the hP22 hexagonal solid solution, and some solid solubility of K_2CO_3 in the low-temperature allotrope $\text{K}_2\text{CrO}_{4(\text{S1})}$ were observed. In ($\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$), emphasis was put on the chrome-glaserite phase (hP14), and both mechanical mixtures of the pre-treated reagents and an equilibrated sample (to which an excess of Na_2CrO_4 or K_2CrO_4 was added subsequently) were investigated in order to best characterize the compositional range of hP14. Finally, the common-cation ternary mixture (55.0 mol% $\text{KCl} + 28.0 \text{ mol\% K}_2\text{CO}_3 + 17.0 \text{ mol\% K}_2\text{CrO}_4$) was also studied by DSC-TGA, thus

permitting to confirm the existence of a ternary eutectic near this composition and around 596°C. All data from the literature and from the present work were reproduced within experimental error limits. The liquid phase and the high-temperature hexagonal solid solution (hP22) were both modelled with the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA), whereas all other solid solutions were modelled with the Compound Energy Formalism (CEF). From the optimized parameters of the binary, ternary common-cation and ternary reciprocal subsystems, it is possible, from the MQMQA, to predict the thermodynamic properties of the multicomponent liquid phase with good accuracy. The thermodynamic model developed in this work is compatible with the FactSage thermochemical software [42] and may be used, along with Gibbs energy minimization software, to calculate phase equilibria in the multicomponent system and study high-temperature corrosion phenomena in the typical temperature range of 600 to 950°C. The addition to this model of the MoO_4^{2-} and $\text{Mo}_2\text{O}_7^{2-}$ anions will be described in a subsequent paper.

7.12 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 apparatus, and Ms. Evguenia Sokolenko for helping locate old articles and for translating them into English.

**CHAPITRE 8 ARTICLE 4 : 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**

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Submitted for publication in Industrial & Engineering Chemistry Research on July 6, 2023

Abstract: A thermodynamic model has been developed for the condensed phases of the salt system (NaCl + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂MoO₄ + Na₂Mo₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇ + K₂O) (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 + Na₂CO₃ + Na₂SO₄ + Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂O + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂O) sub-system was critically evaluated in previous papers. 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 (Na₂CO₃ + Na₂SO₄ + Na₂CrO₄ + Na₂MoO₄ + K₂CO₃ + K₂SO₄ + K₂CrO₄ + [K₂MoO₄]), 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 mol% Na₂MoO₄ + 65 mol% K₂MoO₄) using

SEM-EDS and DSC-TGA, after annealing at 400°C for four weeks.

8.1 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) [14, 57, 58] in the presence of combustion gases (N_2 , CO_2 , CO , O_2 , H_2O , etc.) containing contaminants (SO_2 , Cl_2 , S_2 , HCl , etc.), and corrosive products (Na_2O , K_2O , $NaOH$, KOH , $NaCl$, KCl , etc.) [16, 31]. 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 , Na_2CO_3 , K_2CO_3 , Na_2SO_4 , K_2SO_4 [14, 20, 26, 27, 31], Na_2CrO_4 and K_2CrO_4 [29-31] salts. Further salts are known to promote corrosion, such as Na_2MoO_4 and K_2MoO_4 [30-32] in the solid or liquid form and can dissolve into the previously mentioned salts.

According to Misra's investigation [23], MoO_3 flux created at the interface between the metal and the scale initiates catastrophic corrosion in molybdenum-containing superalloys [23]. The transformation of Na_2SO_4 into Na_2CrO_4 can occur long before the onset of catastrophic corrosion, which is accompanied by the conversion of Na_2CrO_4 to Na_2MoO_4 . A mixture of Na_2MoO_4 and MoO_3 has been attributed to this kind of catastrophic corrosion [23].

Peters et al [260] previously reported the oxidation of Na_2SO_4/Na_2MoO_4 -coated samples, for which a Na_2SO_4 -coated (Ni-15% Cr) alloy exhibited a severe corrosion behavior in the same reaction chamber as the Ni-15Cr-Mo alloys. That is, MoO_3 was dissolving in the salt layer and was then carried into the vapor phase according to the reaction $Na_2SO_4 + MoO_3 = Na_2MoO_4 + SO_3$.

An accurate thermodynamic model is available for the condensed phases of the ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7 + Na_2O + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7 + K_2CrO_4 + K_2Cr_2O_7 + K_2O$) system (diluted in free oxides). The chromium-free version was originally developed by Lindberg et al [39, 41] and then extended in our previous study [75]. The present paper describes the addition of molybdates (Na_2MoO_4 and K_2MoO_4) and dimolybdates ($Na_2Mo_2O_7$

and $K_2Mo_2O_7$) to our existing model. In our previous works [31, 34], an assessment of the thermodynamic properties (standard enthalpy of formation $\Delta H_{298.15\text{ K}}^\circ$ from the elements in their stable standard state at 298.15K and 1 atm, absolute (third law) entropy $S_{298.15\text{ K}}^\circ$ referenced at 298.15K and 1 atm, and heat capacity C_P as a function of temperature) was performed for Na_2MoO_4 , K_2MoO_4 , $Na_2Mo_2O_7$ and $K_2Mo_2O_7$. 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 ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7 + Na_2MoO_4 + Na_2Mo_2O_7 + Na_2O + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7 + K_2CrO_4 + K_2Cr_2O_7 + K_2MoO_4 + K_2Mo_2O_7 + K_2O$) system described in the present article, free oxides are present in dilute amounts since reactions of the type $2 A_2MO_4 = A_2M_2O_7 + A_2O$ (where $A = Na, K$ and $M = Cr, Mo$) are very limited up to above the liquidus temperatures [34].

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 Na_2MoO_4 - and K_2MoO_4 -containing common-cation 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 ($Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4$) and Na, K // Cl, MoO_4 sub-systems. The liquid solution exhibits small deviations from ideality. Hence, predictions in the entire multicomponent 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) are expected to be reasonably accurate.

All calculations and optimizations have been conducted using the FactSage thermochemical software [42].

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

Thermodynamic data ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_p) for the condensed pure compounds of the ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) system were previously selected in references [31, 34, 39, 40, 220], and were directly used in the present study. The thermodynamic data for NaCl and KCl have been evaluated by Chartrand and Pelton [220]. Assessments of the thermodynamic properties of Na_2CO_3 , Na_2SO_4 , K_2CO_3 , K_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$ have been conducted by Lindberg et al [39, 40]. The thermodynamic data for Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, and $\text{K}_2\text{Mo}_2\text{O}_7$ were taken directly from our previous works [31, 34]. Finally, the thermodynamic properties of Na_2O and K_2O were taken directly from the FToxid database in FactSage [42]. 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 8.1. Note that new information is presented only for Na_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, K_2MoO_4 , and $\text{K}_2\text{Mo}_2\text{O}_7$. For all other solid compounds, the corresponding information was given previously [75], 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 8.2.

Table 8.1 Crystal structures and space groups of all relevant pure salt compounds

Pure compound	Allotrope	Crystal structure	Space group	Pearson Symbol / Phase Prototype	Reference
NaCl	NaCl	Cubic	Fm $\bar{3}$ m (225)	cF8 / NaCl	FactSage (FTsalt database) [42]
KCl	KCl	Cubic	Fm $\bar{3}$ m (225)	cF8 / NaCl	FactSage (FTsalt database) [42, 222]
Na ₂ CO ₃	Na ₂ CO ₃ (S ₁)	Monoclinic	C2/m (12)	mS24 / γ -Na ₂ CO ₃ -a	
	Na ₂ CO ₃ (S ₂)	Monoclinic	C2/m (12)	mS24 / β -Na ₂ CO ₃ -b	
	Na ₂ CO ₃ (S ₃)	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	
K ₂ CO ₃	K ₂ CO ₃ (S ₁)	Monoclinic	P2 ₁ /c (14)	mP24 / K ₂ CO ₃	FactSage (FTsalt database) [42]
	K ₂ CO ₃ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	
Na ₂ SO ₄	Na ₂ SO ₄ (S ₃)	Orthorhombic	Fddd (70)	oF56 / Na ₂ SO ₄	FactSage (FTsalt database) [42], [39]
	Na ₂ SO ₄ (S ₁)	Orthorhombic	Cmcm (63)	oS28 / Na ₂ CrO ₄	
	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	P $\bar{1}$ (2)	aP22 / Cd ₂ P ₂ O ₇	FactSage (FTsalt database) [42], [223, 224]
K ₂ SO ₄	K ₂ SO ₄ (S ₁)	Orthorhombic	Pnma (62)	oP28 / K ₂ SO ₄	FactSage (FTsalt database) [42], [39]
	K ₂ SO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	hP22 / K ₂ SO ₄	
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 database) [42], [223]
	K ₂ S ₂ O ₇ (S ₂)	-	-	-	
Na ₂ CrO ₄	Na ₂ CrO ₄ (S ₁)	Orthorhombic	Cmcm (63)	oS28 / Na ₂ CrO ₄	[31, 225]
	Na ₂ CrO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	*	
Na ₂ Cr ₂ O ₇	Na ₂ Cr ₂ O ₇ (S ₁)	Triclinic	P $\bar{1}$ (2)	aP44 / Na ₂ Cr ₂ O ₇	[34, 226, 227]

	Na ₂ Cr ₂ O ₇ (S ₂)	Triclinic	A $\bar{1}$ (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	[31, 228]
	K ₂ CrO ₄ (S ₂)	Hexagonal	P6 ₃ /mmc (194)	*	
K ₂ Cr ₂ O ₇	K ₂ Cr ₂ O ₇ (S ₁)	Triclinic	P $\bar{1}$ (2)	aP44 / K ₂ Cr ₂ O ₇	[34, 223, 229]
	K ₂ Cr ₂ O ₇ (S ₂)	Monoclinic	P2 ₁ /c (14)	-	
Na ₂ MoO ₄	Na ₂ MoO ₄ (S ₁)	Cubic	Fd $\bar{3}$ m (227)	cF56 / MgAl ₂ O ₄	[31, 223, 261]
	Na ₂ MoO ₄ (S ₂)	Orthorhombic	Pbn2 ₁ (33)	-	
	Na ₂ MoO ₄ (S ₃)	Orthorhombic	Fddd (70)	**	
	Na ₂ MoO ₄ (S ₄)	Hexagonal	P6 ₃ /mmc (194)	*	
Na ₂ Mo ₂ O ₇	Na ₂ Mo ₂ O ₇ (S ₁)	Orthorhombic	Cmca D _{2h} ¹⁸ (64)	oS88 / Na ₂ W ₂ O ₇	[34, 262]
	Na ₂ Mo ₂ O ₇ (S ₂)	Monoclinic	-	-	
K ₂ MoO ₄	K ₂ MoO ₄ (S ₁)	Monoclinic	C2/m (12)	mS28 / K ₂ MoO ₄	[31, 223, 263]
	K ₂ MoO ₄ (S ₂)	Orthorhombic	Cmcm (63)	***	
	K ₂ MoO ₄ (S ₃)	Trigonal	P $\bar{3}$ m1 (164)	-	
K ₂ Mo ₂ O ₇	K ₂ Mo ₂ O ₇ (S ₁)	Triclinic	P $\bar{1}$ (2)	aP22 / K ₂ Mo ₂ O ₇	[34, 223, 264]
	K ₂ Mo ₂ O ₇ (S ₂)	Monoclinic (assumption)	P2 ₁ /c or C _{2h} ⁵ – 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 $\text{Na}_2\text{SO}_4(\text{S}_3)$, it was assumed to have the same Pearson symbol / prototype phase (that is, oF56 / Na_2SO_4).

*** The corresponding Pearson symbol / prototype for $\text{K}_2\text{MoO}_4(\text{S}_2)$ is not available to our knowledge. Thus, since this compound has the same crystal structure and space group as $\text{Na}_2\text{CrO}_4(\text{S}_1)$ and $\text{Na}_2\text{SO}_4(\text{S}_1)$, it was assumed to have the same Pearson symbol / prototype phase (that is, oS28 / Na_2CrO_4).

Table 8.2 Thermodynamic properties of solid compounds optimized in the present study

Compound	T Range (K)	$\Delta H_{298.15\text{ K}}^\circ$ (J/mol) ^a	$S_{298.15\text{ K}}^\circ$ (J/mol.K) ^b	C_p (J/mol.K)
$\text{Na}_3\text{ClMoO}_4$	298.15 to 950	-1,872,914.8	248.5426	171.284592 + 0.09489312 T/K
$\text{K}_3\text{Na}(\text{MoO}_4)_2$ (below 513K)	298.15 to 564	-2,980,892.2	380.8465	232.914912 + 0.184602264 T/K + 1,094,534.4 (T/K) ⁻²

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

^b Absolute (third law) entropy.

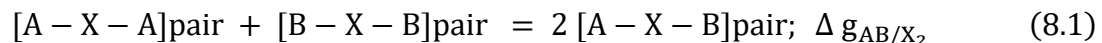
8.3 Thermodynamic model for the liquid phase

The liquid phase of the ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) system (diluted in free oxides) was modeled using the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA) [45]. The cations (Na^+ and K^+ in this work) and the anions (Cl^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_7^{2-}$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_2\text{O}_7^{2-}$ and O^{2-} 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 $\text{Na}_2(\text{MoO}_4)_2$, $\text{NaK}(\text{MoO}_4)_2$, $\text{Na}_2(\text{CO}_3)(\text{MoO}_4)$ or $\text{NaK}(\text{CO}_3)(\text{MoO}_4)$ 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

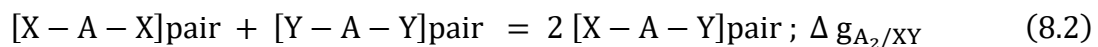
composition (configuration) is obtained by minimizing the Gibbs energy of the liquid solution at a given temperature, pressure and composition, and the equilibrium configuration reflects 1st- and 2nd-nearest-neighbour short-range order among ions.

The model is described in detail in reference [45], and its main features were given in our previous work [75]. A brief summary is provided below.

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



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 [45]). As $\Delta g_{AB/X_2}$ becomes progressively more negative, reaction (8.1) 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 :



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 :



where A and B are two different cations (Na⁺ and K⁺ in this work), and X and Y are two different anions. $\Delta g_{AB/XY}^{\text{exchange}}$ 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, $\Delta g_{NaK/Cl(MoO_4)}^{\text{exchange}}$ for the exchange reaction $NaCl(l) + 0.5 K_2MoO_4(l) \leftrightarrow KCl(l) + 0.5 Na_2MoO_4(l)$ 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 [45] :

$$\frac{1}{2}(ABX_2 + ABY_2 + A_2XY + B_2XY) = 2(ABXY); \Delta g_{AB/XY} \quad (8.4)$$

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 A_2X_2 , A_2Y_2 , B_2X_2 and B_2Y_2 unary quadruplets as follows:

$$\Delta g_{AB/XY} = \Delta g_{AB/XY}^0 + \sum_{i \geq 1} \left[g_{AB/XY(AX)}^i x_{A_2/X_2}^i + g_{AB/XY(BX)}^i x_{B_2/X_2}^i + g_{AB/XY(AY)}^i x_{A_2/Y_2}^i + g_{AB/XY(BY)}^i x_{B_2/Y_2}^i \right] \quad (8.5)$$

The empirical parameters $\Delta g_{AB/XY}^0$ and $g_{AB/XY(AX)}^i$, 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 [45]. 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 ABX_2 and A_2XY quadruplets, respectively. “Default values” of the 2nd-nearest-neighbour (cation-cation or anion-anion) “coordination numbers” for the ABXY quadruplets were proposed previously (equation [23] of reference [45]). These “default values” were used for the $(Na_2SO_4 + K_2SO_4 + Na_2CrO_4 + K_2CrO_4)$, $(NaCl + KCl + Na_2CrO_4 + K_2CrO_4)$ and $(Na_2CO_3 + K_2CO_3 + Na_2CrO_4 + K_2CrO_4)$ ternary reciprocal systems modelled in our previous work [75], and for the $(NaCl + KCl + Na_2MoO_4 + K_2MoO_4)$ ternary reciprocal system modelled in the present study.

It is required to designate all ternary common-cation sub-systems of the $(NaCl + Na_2CO_3 + Na_2SO_4$

+ Na₂S₂O₇ + Na₂CrO₄ + Na₂Cr₂O₇ + Na₂MoO₄ + Na₂Mo₂O₇ + KCl + K₂CO₃ + K₂SO₄ + K₂S₂O₇ + K₂CrO₄ + K₂Cr₂O₇ + K₂MoO₄ + K₂Mo₂O₇) main system as either "symmetric" or "asymmetric" [78]. 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 = CO₃²⁻, 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 (Na₂SO₄ + Na₂CrO₄ + Na₂MoO₄) 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 (8.1)) and $\Delta g_{A_2/XY}$ (reaction (8.2)) 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 [78]. 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) [78].

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

$$G = \sum n_{ij/kl} g_{ij/kl} - T \Delta S^{\text{config}} \quad 8.6$$

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 [45]).

As explained in reference [231], the MQMQA has been improved to address the limitation of the previous model when the Gibbs energy change $\Delta g_{AB/XY}^{\text{exchange}}$ of reaction (8.3) 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 [45]), 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:

$$\zeta_{A/X} = 2Z_{A_2/X_2}^A Z_{A_2/X_2}^X / (Z_{A_2/X_2}^A + Z_{A_2/X_2}^X) \quad (8.7)$$

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 A_2X_2 quadruplets.

Tables 8.3 and 8.4 list, respectively, the values of the 2nd-nearest-neighbour “coordination numbers” and of the newly optimized model parameters for the liquid phase of the $\text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}, \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}, \text{MoO}_4^{2-}, \text{Mo}_2\text{O}_7^{2-}, \text{O}^{2-}$ reciprocal system (diluted in free oxides).

For the $\text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}, \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}, \text{MoO}_4^{2-}, \text{Mo}_2\text{O}_7^{2-}, \text{O}^{2-}$ reciprocal system, the values of $\zeta_{A/X}$ (equation (8.7)) are:

$$\zeta_{A/X} = 4; \quad \zeta_{A/Cl} = 6 \quad (8.8)$$

where $A = \text{Na}^+, \text{K}^+$; and $X = \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}, \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}, \text{MoO}_4^{2-}, \text{Mo}_2\text{O}_7^{2-}, \text{O}^{2-}$.

Table 8.3 2nd-nearest-neighbour “coordination numbers” for the quadruplets ABXY of the newly optimized systems of the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻,

Mo₂O₇²⁻, O²⁻ liquid phase

A	B	X	Y	$Z_{AB/XY}^A$	$Z_{AB/XY}^B$	$Z_{AB/XY}^X$	$Z_{AB/XY}^Y$
Na	Na	Cl	Cl	6	6	6	6
K	K	Cl	Cl	6	6	6	6
Na	Na	CO ₃	CO ₃	3	3	6	6
K	K	CO ₃	CO ₃	3	3	6	6
Na	Na	SO ₄	SO ₄	3	3	6	6
K	K	SO ₄	SO ₄	3	3	6	6
Na	Na	S ₂ O ₇	S ₂ O ₇	3	3	6	6
K	K	S ₂ O ₇	S ₂ O ₇	3	3	6	6
Na	Na	CrO ₄	CrO ₄	3	3	6	6
K	K	CrO ₄	CrO ₄	3	3	6	6
Na	Na	Cr ₂ O ₇	Cr ₂ O ₇	3	3	6	6
K	K	Cr ₂ O ₇	Cr ₂ O ₇	3	3	6	6
Na	Na	MoO ₄	MoO ₄	3	3	6	6
K	K	MoO ₄	MoO ₄	3	3	6	6
Na	Na	Mo ₂ O ₇	Mo ₂ O ₇	3	3	6	6
K	K	Mo ₂ O ₇	Mo ₂ O ₇	3	3	6	6
Na	Na	O	O	3	3	6	6
K	K	O	O	3	3	6	6

Na	Na	Cl	MoO ₄	4	4	4	8
K	K	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
K	K	CO ₃	MoO ₄	3	3	6	6
K	K	SO ₄	MoO ₄	3	3	6	6
K	K	CrO ₄	MoO ₄	3	3	6	6
Na	K	MoO ₄	MoO ₄	3	3	6	6
K	K	Cr ₂ O ₇	Mo ₂ O ₇	3	3	6	6
Na	Na	MoO ₄	Mo ₂ O ₇	3	3	6	6
K	K	MoO ₄	Mo ₂ O ₇	3	3	6	6

The 2nd-nearest-neighbour "coordination numbers" for the ABXY quadruplets of the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, O²⁻ liquid phase were given previously by Lindberg et al [39, 41] and in our previous work [75], and they were directly used in the present work.

Table 8.4 Model parameters optimized in the present work for the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻, Mo₂O₇²⁻, O²⁻ liquid phase (diluted in free oxides)

System	Model parameter (J/mol)
(NaCl + Na ₂ MoO ₄)	$\Delta g_{\text{Na}_2/(\text{Cl})(\text{MoO}_4)} = 300.0 \chi_{(\text{Cl})(\text{MoO}_4)}$
(KCl + K ₂ MoO ₄)	$\Delta g_{\text{K}_2/(\text{Cl})(\text{MoO}_4)} = -1,000.0 + 500.0 \chi_{(\text{Cl})(\text{MoO}_4)} - 200.0 \chi_{(\text{MoO}_4)(\text{Cl})}$

(Na ₂ CO ₃ + Na ₂ MoO ₄)	$\Delta g_{\text{Na}_2/(\text{CO}_3)(\text{MoO}_4)} = 700.0$
(K ₂ CO ₃ + K ₂ MoO ₄)	$\Delta g_{\text{K}_2/(\text{CO}_3)(\text{MoO}_4)} = 1,150.0 + 900.0\chi_{(\text{MoO}_4)(\text{CO}_3)}$
(Na ₂ SO ₄ + Na ₂ MoO 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 ₂ SO ₄ + K ₂ MoO ₄)	$\Delta g_{\text{K}_2/(\text{SO}_4)(\text{MoO}_4)} = 500.0 + 800.0\chi_{(\text{SO}_4)(\text{MoO}_4)}$
(Na ₂ CrO ₄ + Na ₂ MoO ₄)	$\Delta g_{\text{Na}_2/(\text{CrO}_4)(\text{MoO}_4)} = 1,000.0 - 1,000.0\chi_{(\text{CrO}_4)(\text{MoO}_4)} + 1,200.0\chi_{(\text{MoO}_4)(\text{CrO}_4)}$
(K ₂ CrO ₄ + K ₂ MoO ₄)	$\Delta g_{\text{K}_2/(\text{CrO}_4)(\text{MoO}_4)} = 2,000.0 + 1,500.0\chi_{(\text{CrO}_4)(\text{MoO}_4)}$
(Na ₂ MoO ₄ + K ₂ MoO ₄)	$\Delta g_{\text{NaK}/(\text{MoO}_4)_2} = -500.0 + 750.0\chi_{\text{NaK}}$
(Na ₂ MoO ₄ + Na ₂ Mo ₂ O 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 ₂ MoO ₄ + KCl + K ₂ MoO ₄)	$\Delta g_{\text{NaK}/(\text{Cl})(\text{MoO}_4)} = 7,000.0\chi_{\text{K}_2/(\text{MoO}_4)_2}$

8.4 Thermodynamic model for the solid solutions

Several solid solutions were modeled in the Na⁺, K⁺ // Cl⁻, CO₃²⁻, SO₄²⁻, S₂O₇²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻, Mo₂O₇²⁻-main system. Table 8.5 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 [75], 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 (K₂MoO₄(s₃)-ht-ss, cF56, and Na₂MoO₄(s₂)-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 [45] was used to model this reciprocal solid solution, with two sublattices (a cationic one and an anionic one). As explained

previously [75], the MQM is more suited than the Compound Energy Formalism (CEF) [46-48] to model complex solid solutions such as $(\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4)$ dissolving divalent cation sulfates like CaSO_4 , ZnSO_4 and PbSO_4 . In particular, in a recent work [235], the MQM was used to add ZnSO_4 and PbSO_4 as solutes in the high-temperature $(\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4)$ 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 CO_3^{2-} , SO_4^{2-} , CrO_4^{2-} , and MoO_4^{2-} as the anions). All other solid solutions exhibited limited solubility, and were modeled with the CEF [46-48]. In most cases, two sublattices were required. However, three sublattices were used for the molybdenum-glaserite phase $\text{K}_3\text{Na}(\text{MoO}_4)_2$, which exhibits significant non-stoichiometry at temperatures above 240°C [44].

As an example, let us consider the aP44 solid solution which consists of the triclinic low-temperature allotropes $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S1})$, $\text{K}_2\text{Cr}_2\text{O}_7(\text{S1})$, and $\text{K}_2\text{Mo}_2\text{O}_7(\text{S1})$ (mutually soluble) dissolving $\text{Na}_2\text{Mo}_2\text{O}_7$. The sublattice structure $(\text{Na}^+, \text{K}^+)_2(\text{Cr}_2\text{O}_7^{2-}, \text{Mo}_2\text{O}_7^{2-})$ was used, where Na^+ and K^+ reside on the cationic sublattice C while $\text{Cr}_2\text{O}_7^{2-}$ and $\text{Mo}_2\text{O}_7^{2-}$ reside on the anionic sublattice A. The molar Gibbs energy of the solution is given by the following expression :

$$\begin{aligned}
 G_m = & y_{\text{Na}^+}^{\text{C}} y_{\text{Cr}_2\text{O}_7^{2-}}^{\text{A}} G_{\text{Na}^+:\text{Cr}_2\text{O}_7^{2-}}^{\circ} + y_{\text{K}^+}^{\text{C}} y_{\text{Cr}_2\text{O}_7^{2-}}^{\text{A}} G_{\text{K}^+:\text{Cr}_2\text{O}_7^{2-}}^{\circ} + y_{\text{Na}^+}^{\text{C}} y_{\text{Mo}_2\text{O}_7^{2-}}^{\text{A}} G_{\text{Na}^+:\text{Mo}_2\text{O}_7^{2-}}^{\circ} \\
 & + y_{\text{K}^+}^{\text{C}} y_{\text{Mo}_2\text{O}_7^{2-}}^{\text{A}} G_{\text{K}^+:\text{Mo}_2\text{O}_7^{2-}}^{\circ} + 2RT(y_{\text{Na}^+}^{\text{C}} \ln y_{\text{Na}^+}^{\text{C}} + y_{\text{K}^+}^{\text{C}} \ln y_{\text{K}^+}^{\text{C}}) + \\
 & RT(y_{\text{Cr}_2\text{O}_7^{2-}}^{\text{A}} \ln y_{\text{Cr}_2\text{O}_7^{2-}}^{\text{A}} + y_{\text{Mo}_2\text{O}_7^{2-}}^{\text{A}} \ln y_{\text{Mo}_2\text{O}_7^{2-}}^{\text{A}}) + G^{\text{E}}
 \end{aligned} \tag{8.9}$$

The first four terms give the reference Gibbs energy of the solution, where $y_{\text{Na}^+}^{\text{C}}$ and $y_{\text{K}^+}^{\text{C}}$ are the site fractions of Na^+ and K^+ on the cationic sublattice C, and $y_{\text{Cr}_2\text{O}_7^{2-}}^{\text{A}}$ and $y_{\text{Mo}_2\text{O}_7^{2-}}^{\text{A}}$ are the site fractions of $\text{Cr}_2\text{O}_7^{2-}$ and $\text{Mo}_2\text{O}_7^{2-}$ on the anionic sublattice A. The standard molar Gibbs energies of the end-member components $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$ and $\text{K}_2\text{Mo}_2\text{O}_7$ are represented by $G_{\text{Na}^+:\text{Cr}_2\text{O}_7^{2-}}^{\circ}$, $G_{\text{K}^+:\text{Cr}_2\text{O}_7^{2-}}^{\circ}$, $G_{\text{Na}^+:\text{Mo}_2\text{O}_7^{2-}}^{\circ}$ and $G_{\text{K}^+:\text{Mo}_2\text{O}_7^{2-}}^{\circ}$, respectively.

Since the cations and anions are assumed to be randomly distributed on their respective sublattice, as in the Temkin-type [236], the fifth and sixth terms in equation (8.9) correspond to the ideal entropy of mixing. The final term represents the molar excess Gibbs energy and is given by:

$$\begin{aligned}
G^E = & y_{Na^+}^C y_{K^+}^C y_{Cr_2O_7^{2-}}^A L_{Na^+, K^+: Cr_2O_7^{2-}} + y_{Na^+}^C y_{K^+}^C y_{Mo_2O_7^{2-}}^A L_{Na^+, K^+: Mo_2O_7^{2-}} \\
& + y_{Na^+}^C y_{Cr_2O_7^{2-}}^A y_{Mo_2O_7^{2-}}^A L_{Na^+: Cr_2O_7^{2-}, Mo_2O_7^{2-}} + y_{K^+}^C y_{Cr_2O_7^{2-}}^A y_{Mo_2O_7^{2-}}^A L_{K^+: Cr_2O_7^{2-}, Mo_2O_7^{2-}} \\
& + y_{Na^+}^C y_{K^+}^C y_{Cr_2O_7^{2-}}^A y_{Mo_2O_7^{2-}}^A L_{Na^+, K^+: Cr_2O_7^{2-}, Mo_2O_7^{2-}} \quad (8.10)
\end{aligned}$$

In equation (8.10), 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 $L_{i \geq 0}^i (y_A - y_B)^i$ as a function of site fractions are generally employed.

Table 8.5 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

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:

$$g_{Na_2CO_3}^\circ = g_{Na_2CO_{3(S3)}}^\circ$$

$$g_{K_2CO_3}^\circ = g_{K_2CO_{3(S2)}}^\circ$$

$$g_{Na_2SO_4}^\circ = g_{Na_2SO_{4(S2)}}^\circ$$

$$g_{K_2SO_4}^\circ = g_{K_2SO_{4(S2)}}^\circ$$

$$g_{Na_2CrO_4}^\circ = g_{Na_2CrO_{4(S2)}}^\circ$$

$$g_{K_2CrO_4}^\circ = g_{K_2CrO_{4(S2)}}^\circ$$

$$g_{\text{Na}_2\text{MoO}_4}^{\circ} = g_{\text{Na}_2\text{MoO}_4(\text{S}_4)}^{\circ}$$

$$g_{\text{K}_2\text{MoO}_4}^{\circ} = g_{\text{K}_2\text{MoO}_4(\text{S}_3)}^{\circ} + 10 \text{ (J/mol)}$$

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 $A = \text{Na}^+$, K^+ and $X = \text{CO}_3^{2-}$, SO_4^{2-} , CrO_4^{2-} and MoO_4^{2-}).

The following interaction parameters for $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4)$, $(\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4)$, $(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3)$, $(\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4)$ and Na, K // CO_3 , SO_4 were obtained previously:

$$\Delta g_{\text{Na}_2/(\text{CO}_3)(\text{SO}_4)} = 1,106.7 + 1,060.0 Y_{\text{CO}_3} \text{ (J/mol)} \quad [40] \text{ (This is a Bragg-Williams type term and } Y_{\text{CO}_3} \text{ is the equivalent site fraction of } \text{CO}_3\text{)}$$

$$\Delta g_{\text{K}_2/(\text{CO}_3)(\text{SO}_4)} = 1,571.7 + 105.0 Y_{\text{CO}_3} \text{ (J/mol)} \quad [40]$$

$$\Delta g_{\text{NaK}/(\text{CO}_3)_2} = 4,935.0 - 2,928.2 Y_{\text{K}} \text{ (J/mol)} \quad [40]$$

$$\Delta g_{\text{NaK}/(\text{SO}_4)_2} = 3,040.4 + (2,370.9 - 3.1241 \times T) Y_{\text{K}} \text{ (J/mol)} \quad [39, 40]$$

$$\Delta g_{\text{NaK}/(\text{CO}_3)(\text{SO}_4)} = 1,401.3 \text{ (J/mol)} \quad [40]$$

The following interaction parameters for $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4)$, $(\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$, $(\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4)$, $(\text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4)$ and $(\text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4)$ were obtained in our previous work [75]:

$$\Delta g_{\text{Na}_2/(\text{CO}_3)(\text{CrO}_4)} = 8,000.0 - 1,800.0 Y_{\text{CrO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{K}_2/(\text{CO}_3)(\text{CrO}_4)} = 5,600.0 - 800.0 Y_{\text{CrO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{Na}_2/(\text{SO}_4)(\text{CrO}_4)} = 800.0 \text{ (J/mol)}$$

$$\Delta g_{\text{K}_2/(\text{SO}_4)(\text{CrO}_4)} = 1,000.0 - 500.0 Y_{\text{SO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{NaK}/(\text{CrO}_4)_2} = 2,700.0 + (2,000.0 - 2.4500 \times T) Y_{\text{K}} \text{ (J/mol)}$$

The following MoO_4 -based interaction parameters were obtained in the present work:

$$\Delta g_{\text{Na}_2/(\text{CO}_3)(\text{MoO}_4)} = 100,000.0 \text{ (J/mol)}$$

$$\Delta g_{\text{K}_2/(\text{CO}_3)(\text{MoO}_4)} = 100,000.0 \text{ (J/mol)}$$

$$\Delta g_{\text{Na}_2/(\text{SO}_4)(\text{MoO}_4)} = 500.0 - 5,000.0 Y_{\text{SO}_4} - 1,600.0 Y_{\text{MoO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{Na}_2/(\text{CrO}_4)(\text{MoO}_4)} = 500.0 Y_{\text{CrO}_4} + 2,500.0 Y_{\text{MoO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{K}_2/(\text{SO}_4)(\text{MoO}_4)} = 2,000.0 + 2,000.0 Y_{\text{SO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{K}_2/(\text{CrO}_4)(\text{MoO}_4)} = 650.0 + 3,200.0 Y_{\text{CrO}_4} + 2,060.0 Y_{\text{MoO}_4} \text{ (J/mol)}$$

$$\Delta g_{\text{NaK}/(\text{MoO}_4)_2} = 3,500.0 \text{ (J/mol)}$$

Solid solution K₂MoO₄(s3)-ht-ss

Trigonal high-temperature allotrope K₂MoO₄(s3) dissolving K₂SO₄, K₂CrO₄, Na₂MoO₄, Na₂SO₄ and Na₂CrO₄

P $\bar{3}$ m1 space group

Sublattice structure: (K⁺, Na⁺)₂(MoO₄²⁻, SO₄²⁻, CrO₄²⁻)

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

$$g_{\text{K}_2\text{MoO}_4}^\circ = g_{\text{K}_2\text{MoO}_4(\text{s3})}^\circ$$

$$g_{\text{K}_2\text{SO}_4}^\circ = g_{\text{K}_2\text{SO}_4(\text{s2})}^\circ + 6,129.6 \text{ (J/mol)}$$

$$g_{\text{K}_2\text{CrO}_4}^\circ = g_{\text{K}_2\text{CrO}_4(\text{s2})}^\circ + 7,322.0 \text{ (J/mol)}$$

$$g_{\text{Na}_2\text{MoO}_4}^\circ = g_{\text{Na}_2\text{MoO}_4(\text{s4})}^\circ + 10,250.8 \text{ (J/mol)}$$

$$g_{\text{Na}_2\text{SO}_4}^{(1)\circ} = g_{\text{Na}_2\text{SO}_4(\text{s2})}^\circ + 6,129.6 \text{ (J/mol)}$$

$$g_{\text{Na}_2\text{CrO}_4}^{(2)\circ} = g_{\text{Na}_2\text{CrO}_4(\text{s2})}^\circ + 7,322.0 \text{ (J/mol)}$$

Solid solution oS28

Orthorhombic low-temperature allotropes Na₂CrO₄(s1), Na₂SO₄(s1) and K₂MoO₄(s2) mutually soluble, and dissolving K₂CrO₄, Na₂CO₃, K₂SO₄, K₂CO₃ and Na₂MoO₄

Cmcm space group

Sublattice structure: (Na⁺, K⁺)₂(SO₄²⁻, CrO₄²⁻, MoO₄²⁻, CO₃²⁻)

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

$$g_{\text{Na}_2\text{CrO}_4}^\circ = g_{\text{Na}_2\text{CrO}_4(\text{s1})}^\circ$$

$$g_{\text{Na}_2\text{SO}_4}^{\circ} = g_{\text{Na}_2\text{SO}_4(\text{S1})}^{\circ}$$

$$g_{\text{Na}_2\text{MoO}_4}^{\circ} = g_{\text{Na}_2\text{MoO}_4(\text{S3})}^{\circ} + 6,276.0 \text{ (J/mol)}$$

$$g_{\text{Na}_2\text{CO}_3}^{\circ} = g_{\text{Na}_2\text{CO}_3(\text{S2})}^{\circ} + 7,112.8 \text{ (J/mol) [40]}$$

$$g_{\text{K}_2\text{CrO}_4}^{\circ} = g_{\text{K}_2\text{CrO}_4(\text{S1})}^{\circ} + (33,472.0 - 7.7404 \times T) \text{ (J/mol) [75]}$$

$$g_{\text{K}_2\text{SO}_4}^{\circ} = g_{\text{K}_2\text{SO}_4(\text{S1})}^{\circ} + 33,472.0 \text{ (J/mol) [40]}$$

$$g_{\text{K}_2\text{MoO}_4}^{\circ} = g_{\text{K}_2\text{MoO}_4(\text{S2})}^{\circ}$$

$$g_{\text{K}_2\text{CO}_3}^{\circ} = g_{\text{K}_2\text{CO}_3(\text{S1})}^{\circ} + 4,184.0 \text{ (J/mol) [40]}$$

The following Redlich-Kister interaction parameter for ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$) was obtained previously:

$$L_{\text{Na}/(\text{CO}_3)(\text{SO}_4)}^0 = 3,347.2 \text{ (J/mol) [40]}$$

The following Redlich-Kister interaction parameters for ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4$) and ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$) were obtained in our previous work [75]:

$$L_{\text{Na}/(\text{CrO}_4)(\text{CO}_3)}^0 = 100,000.0 \text{ (J/mol)}$$

$$L_{\text{Na}/(\text{CrO}_4)(\text{SO}_4)}^0 = 3,000.0 \text{ (J/mol)}$$

The following MoO_4 -based Redlich-Kister interaction parameters were obtained in the present work:

$$L_{\text{K}/(\text{CO}_3)(\text{MoO}_4)}^0 = 100,000.0 \text{ (J/mol)}$$

$$L_{\text{Na}/(\text{SO}_4)(\text{MoO}_4)}^0 = 100,000.0 \text{ (J/mol)}$$

$$L_{\text{Na}/(\text{CrO}_4)(\text{MoO}_4)}^0 = 500.0 \text{ (J/mol)}$$

$$L_{\text{K}/(\text{SO}_4)(\text{MoO}_4)}^0 = -26,000.0 \text{ (J/mol)}$$

$$L_{\text{K}/(\text{CrO}_4)(\text{MoO}_4)}^0 = -19,200.0 \text{ (J/mol)}$$

$$L_{\text{NaK}/(\text{MoO}_4)}^0 = 6,200.0 \text{ (J/mol)}$$

Solid solution oP28

Orthorhombic low-temperature allotropes $\text{K}_2\text{CrO}_{4(\text{S1})}$ and $\text{K}_2\text{SO}_{4(\text{S1})}$ mutually soluble, and dissolving Na_2CrO_4 , K_2CO_3 , Na_2SO_4 , Na_2CO_3 , K_2MoO_4 and Na_2MoO_4

Pnma space group

Sublattice structure: $(\text{K}^+, \text{Na}^+)_2(\text{SO}_4^{2-}, \text{CrO}_4^{2-}, \text{MoO}_4^{2-}, \text{CO}_3^{2-})$

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

$$g_{\text{K}_2\text{CrO}_4}^\circ = g_{\text{K}_2\text{CrO}_{4(\text{S1})}}^\circ$$

$$g_{\text{K}_2\text{SO}_4}^\circ = g_{\text{K}_2\text{SO}_{4(\text{S1})}}^\circ$$

$$g_{\text{K}_2\text{CO}_3}^\circ = g_{\text{K}_2\text{CO}_{3(\text{S1})}}^\circ + 209.2 \text{ (J/mol) [40]}$$

$$g_{\text{K}_2\text{MoO}_4}^\circ = g_{\text{K}_2\text{MoO}_{4(\text{S3})}}^\circ + 13,388.8 \text{ (J/mol)}$$

$$g_{\text{Na}_2\text{CrO}_4}^\circ = g_{\text{Na}_2\text{CrO}_{4(\text{S1})}}^\circ + (13,388.8 + 2.7196 \times T) \text{ (J/mol) [75]}$$

$$g_{\text{Na}_2\text{SO}_4}^\circ = g_{\text{Na}_2\text{SO}_{4(\text{S1})}}^\circ + (29,288.0 - 20.9200 \times T) \text{ (J/mol) [40]}$$

$$g_{\text{Na}_2\text{CO}_3}^\circ = g_{\text{Na}_2\text{CO}_{3(\text{S1})}}^\circ + 20,920.0 \text{ (J/mol) [40]}$$

$$g_{\text{Na}_2\text{MoO}_4}^{(3)\circ} = g_{\text{Na}_2\text{MoO}_{4(\text{S1})}}^\circ + 20,920.0 \text{ (J/mol)}$$

The following Redlich-Kister interaction parameters for $(\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4)$ were obtained previously:

$$L_{\text{K}/(\text{CO}_3)(\text{SO}_4)}^0 = 3,765.6 \text{ (J/mol) [40]}$$

$$L_{\text{K}/(\text{CO}_3)(\text{SO}_4)}^1 = -2,008.3 \text{ (J/mol) [40]}$$

The following Redlich-Kister interaction parameters for $(\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$ and $(\text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4)$ were obtained in our previous work [75]:

$$L_{\text{K}/(\text{CO}_3)(\text{CrO}_4)}^0 = 17,500.0 \text{ (J/mol)}$$

$$L_{\text{K}/(\text{CO}_3)(\text{CrO}_4)}^1 = 3,000.0 \text{ (J/mol)}$$

$$L_{\text{K}/(\text{CrO}_4)(\text{SO}_4)}^0 = 1,800.0 \text{ (J/mol)}$$

Glaserite solid solution hP14

Solid $\text{K}_3\text{Na}(\text{SO}_4)_2$, $\text{K}_3\text{Na}(\text{CrO}_4)_2$ and $\text{K}_3\text{Na}(\text{MoO}_4)_2$ mutually soluble, and dissolving Na^+

$P\bar{3}m1$ 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:

$$g_{K_3Na(SO_4)_2}^\circ = 1.5 \times g_{K_2SO_4(S1)}^\circ + 0.5 \times g_{Na_2SO_4(S2)}^\circ - 10,878.4 + 9.7906 \times T \text{ (J/mol) [39]}$$

$$g_{Na_3Na(SO_4)_2}^\circ = 2 \times g_{Na_2SO_4(S2)}^\circ + 16,736.0 - 10.7110 \times T \text{ (J/mol) [39]}$$

$$g_{K_3Na(CrO_4)_2}^\circ = 1.5 \times g_{K_2CrO_4(S1)}^\circ + 0.5 \times g_{Na_2CrO_4(S1)}^\circ - 17,154.4 + 9.4140 \times T \text{ (J/mol) [75]}$$

$$g_{Na_3Na(CrO_4)_2}^\circ = 2 \times g_{Na_2CrO_4(S1)}^\circ + 12,970.4 - 8.1588 \times T \text{ (J/mol) [75]}$$

$$g_{K_3Na(MoO_4)_2}^\circ = 1.5 \times g_{K_2MoO_4(S3)}^\circ + 0.5 \times g_{Na_2MoO_4(S4)}^\circ - 10,460.0 \text{ (J/mol)}$$

$$g_{Na_3Na(MoO_4)_2}^\circ = 2 \times g_{Na_2MoO_4(S4)}^\circ + 23,012.0 \text{ (J/mol)}$$

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:

$$g_{Na_2SO_4}^\circ = g_{Na_2SO_4(S3)}^\circ$$

$$g_{K_2SO_4}^\circ = g_{K_2SO_4(S1)}^\circ + 66,944.0 \text{ (J/mol) [75]}$$

$$g_{Na_2CrO_4}^\circ = g_{Na_2CrO_4(S1)}^\circ + 4,100.3 \text{ (J/mol) [75]}$$

$$g_{K_2CrO_4}^\circ = g_{K_2CrO_4(S1)}^\circ + 66,944.0 \text{ (J/mol) [75]}$$

$$g_{Na_2MoO_4}^\circ = g_{Na_2MoO_4(S3)}^\circ$$

$$g_{K_2MoO_4}^\circ = g_{K_2MoO_4(S3)}^\circ + (-7,531.2 + 37.0284 \times T) \text{ (J/mol)}$$

The following MoO_4 -based Redlich-Kister interaction parameters were obtained in the present work:

$$L_{\text{NaK/MoO}_4}^0 = -18,000.0 \text{ (J/mol)}$$

$$L_{\text{NaK/MoO}_4}^1 = 15,000.0 \text{ (J/mol)}$$

$$L_{\text{Na}/(\text{SO}_4)(\text{MoO}_4)}^0 = 100,000.0 \text{ (J/mol)}$$

$$L_{\text{Na}/(\text{CrO}_4)(\text{MoO}_4)}^0 = 100,000.0 \text{ (J/mol)}$$

Solid solution cF56

Cubic low-temperature allotrope $\text{Na}_2\text{MoO}_{4(\text{S1})}$ dissolving Na_2SO_4 and Na_2CrO_4

$\text{Fd}\bar{3}\text{m}$ space group

Sublattice structure: $(\text{Na}^+)_2(\text{MoO}_4^{2-}, \text{SO}_4^{2-}, \text{CrO}_4^{2-})$

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

$$g_{\text{Na}_2\text{MoO}_4}^\circ = g_{\text{Na}_2\text{MoO}_{4(\text{S1})}}^\circ$$

$$g_{\text{Na}_2\text{SO}_4}^\circ = g_{\text{Na}_2\text{SO}_{4(\text{S1})}}^\circ + (8,368.0 + 16.7360 \times T) \text{ (J/mol)}$$

$$g_{\text{Na}_2\text{CrO}_4}^\circ = g_{\text{Na}_2\text{CrO}_{4(\text{S1})}}^\circ + (8,368.0 + 16.7360 \times T) \text{ (J/mol)}$$

Solid solution $\text{Na}_2\text{MoO}_{4(\text{S2})}$ -ss-rich

Orthorhombic intermediate-temperature allotrope $\text{Na}_2\text{MoO}_{4(\text{S2})}$ dissolving Na_2SO_4 and Na_2CrO_4

$\text{Pbn}2_1$ space group

Sublattice structure: $(\text{Na}^+)_2(\text{MoO}_4^{2-}, \text{SO}_4^{2-}, \text{CrO}_4^{2-})$

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

$$g_{\text{Na}_2\text{MoO}_4}^\circ = g_{\text{Na}_2\text{MoO}_{4(\text{S2})}}^\circ$$

$$g_{\text{Na}_2\text{SO}_4}^\circ = g_{\text{Na}_2\text{SO}_{4(\text{S2})}}^\circ + (1,046.0 + 16.7360 \times T) \text{ (J/mol)}$$

$$g_{\text{Na}_2\text{CrO}_4}^\circ = g_{\text{Na}_2\text{CrO}_{4(\text{S2})}}^\circ + (1,046.0 + 16.7360 \times T) \text{ (J/mol)}$$

Solid solution aP22

Triclinic allotropes $\text{Na}_2\text{S}_2\text{O}_7$ and $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{S2})}$ mutually soluble, and dissolving $\text{K}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7$

$A\bar{1}$ space group

Sublattice structure: $(\text{Na}^+, \text{K}^+)_2(\text{S}_2\text{O}_7^{2-}, \text{Cr}_2\text{O}_7^{2-})$

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

$$g_{\text{Na}_2\text{S}_2\text{O}_7}^\circ = g_{\text{Na}_2\text{S}_2\text{O}_7(\text{S})}^\circ$$

$$g_{\text{K}_2\text{S}_2\text{O}_7}^\circ = g_{\text{K}_2\text{S}_2\text{O}_7(\text{S}_2)}^\circ + 29,288.0 \text{ (J/mol) [39]}$$

$$g_{\text{Na}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_2)}^\circ$$

$$g_{\text{K}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{K}_2\text{Cr}_2\text{O}_7(\text{S}_2)}^\circ + 7,531.2 + 5.6484 \times T \text{ (J/mol) [75]}$$

Solid solution aP44

Triclinic low-temperature allotropes $\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_1)$, $\text{K}_2\text{Cr}_2\text{O}_7(\text{S}_1)$ and $\text{K}_2\text{Mo}_2\text{O}_7(\text{S}_1)$ mutually soluble, and dissolving $\text{Na}_2\text{Mo}_2\text{O}_7$

$P\bar{1}$ space group

Sublattice structure: $(\text{K}^+, \text{Na}^+)_2(\text{Cr}_2\text{O}_7^{2-}, \text{Mo}_2\text{O}_7^{2-})$

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

$$g_{\text{Na}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{Na}_2\text{Cr}_2\text{O}_7(\text{S}_1)}^\circ$$

$$g_{\text{K}_2\text{Cr}_2\text{O}_7}^\circ = g_{\text{K}_2\text{Cr}_2\text{O}_7(\text{S}_1)}^\circ$$

$$g_{\text{K}_2\text{Mo}_2\text{O}_7}^\circ = g_{\text{K}_2\text{Mo}_2\text{O}_7(\text{S}_1)}^\circ$$

$$g_{\text{Na}_2\text{Mo}_2\text{O}_7}^\circ = g_{\text{Na}_2\text{Mo}_2\text{O}_7(\text{S}_1)}^\circ + 11,296.8 + 3.8911 \times T \text{ (J/mol)}$$

The following Redlich-Kister interaction parameter for $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Cr}_2\text{O}_7)$ was obtained in our previous study [75] :

$$L_{\text{NaK/Cr}_2\text{O}_7}^0 = 20,000.0 \text{ (J/mol)}$$

The following Mo_2O_7 -based Redlich-Kister interaction parameter was obtained in the present work:

$$L_{\text{K}/(\text{Cr}_2\text{O}_7)(\text{Mo}_2\text{O}_7)}^0 = 4,500.0 \text{ (J/mol)}$$

Solid solution $K_2Cr_2O_7(s.s)$

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:

$$g_{K_2Cr_2O_7}^\circ = g_{K_2Cr_2O_{7(s2)}}^\circ$$

$$g_{Na_2Cr_2O_7}^\circ = g_{Na_2Cr_2O_{7(s2)}}^\circ + 11,296.8 + 3.8911 \times T \text{ (J/mol) [75]}$$

$$g_{K_2Mo_2O_7}^\circ = g_{K_2Mo_2O_{7(s2)}}^\circ$$

$$g_{Na_2Mo_2O_7}^{(5)\circ} = g_{Na_2Mo_2O_{7(s2)}}^\circ + 11,296.8 + 3.8911 \times T \text{ (J/mol)}$$

The following Mo_2O_7 -based Redlich-Kister interaction parameter was obtained in the present work:

$$L_{K/(Cr_2O_7)(Mo_2O_7)}^0 = 4,500.0 \text{ (J/mol)}$$

Rocksalt solid solution cF8

Cubic NaCl and KCl mutually soluble

$Fm\bar{3}m$ space group

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

$$g_{NaCl}^\circ = g_{NaCl(s)}^\circ$$

$$g_{KCl}^\circ = g_{KCl(s)}^\circ$$

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

$$L_{NaK/Cl}^0 = 15,972.0 + 32.7960 \times T - 5.593 \times T \times \ln(T) \text{ (J/mol) [237]}$$

$$L_{NaK/Cl}^1 = 1,639.0 \text{ (J/mol) [237]}$$

^{(1),(2)} The "end-members" Na_2SO_4 and Na_2CrO_4 were added to the $K_2MoO_{4(s3)}$ -ht-ss solid solution. The corresponding Gibbs energies are those of $Na_2SO_{4(s2)}$ and $Na_2CrO_{4(s2)}$ augmented by a positive Gibbs energy, respectively. The latter were assumed to

be identical to those for the “end-members” K_2SO_4 (i.e. 6,129.6 J/mol) and K_2CrO_4 (i.e. 7,322.0 J/mol), respectively. The “end-members” Na_2SO_4 and Na_2CrO_4 are only required for calculations in the K, Na // MoO_4 , SO_4 and K, Na // MoO_4 , CrO_4 reciprocal systems, respectively, and higher-order systems.

⁽³⁾ The “end-member” Na_2MoO_4 was added to the oP28 solid solution. The corresponding Gibbs energy is that of $\text{Na}_2\text{MoO}_4(\text{s}_1)$ augmented by a positive Gibbs energy. As a first approximation, the latter was assumed to be identical to that for the “end-member” Na_2CO_3 (i.e. 20,920.0 J/mol). The “end-member” Na_2MoO_4 is only required for calculations in the K, Na // SO_4 , MoO_4 and K, Na // CrO_4 , MoO_4 reciprocal systems, and higher-order systems.

^{(4),(5)} The “end-member” $\text{Na}_2\text{Mo}_2\text{O}_7$ was added to both of the solid solutions aP44 and $\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s})$. The corresponding Gibbs energies are those of $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_1)$ and $\text{Na}_2\text{Mo}_2\text{O}_7(\text{s}_2)$ augmented by a positive Gibbs energy, respectively. As a first approximation, the latter were assumed to be identical to that for the “end-member” $\text{Na}_2\text{Cr}_2\text{O}_7$ in the $\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s})$ solid solution (that is, $11,296.8 + 3.8911 \times T$ J/mol), which was obtained in our previous work. The “end-member” $\text{Na}_2\text{Mo}_2\text{O}_7$ is only required for calculations in the K, Na // Cr_2O_7 , Mo_2O_7 ternary reciprocal system and higher-order systems.

8.5 Experimental procedure

8.5.1 DSC-TGA

Materials and measurements

The present work was carried out using high purity gases (99.999% pure Ar, 99.999% pure N_2 , and 99.999% pure CO_2) from Oy Linde Gas AB (Finland). For all initial solid reagents (Na_2CO_3 , Na_2SO_4 , K_2SO_4 , $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$, K_2CrO_4 , Na_2MoO_4 , and K_2MoO_4), the supplier’s name, CAS number and purity are reported in Table 8.6.

Table 8.6 Purity and origin of the solid reagents used in our experiments

Chemical formula	Supplier	CAS number	Purity (%)
Na_2CO_3	Sigma-Aldrich	497-19-8	≥ 99.95
Na_2SO_4	Sigma-Aldrich	7757-82-6	≥ 99.0

K_2SO_4	Sigma-Aldrich	7778-80-5	≥ 99.0
$Na_2CrO_4 \cdot 4H_2O$	Sigma-Aldrich	10034-82-9	99.0
K_2CrO_4	Alfa-Aesar	7789-00-6	99.9
Na_2MoO_4	Sigma-Aldrich	7631-95-0	99.9
K_2MoO_4	Sigma-Aldrich	13446-49-6	98

The binary common-ion sub-systems ($Na_2CO_3 + Na_2MoO_4$), ($K_2SO_4 + K_2MoO_4$), ($Na_2CrO_4 + Na_2MoO_4$), ($K_2CrO_4 + K_2MoO_4$) and ($Na_2MoO_4 + K_2MoO_4$) 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 ($Na_2SO_4 + Na_2MoO_4$) and ($K_2SO_4 + K_2MoO_4$). 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 8.6.

A detailed description of the calibration of the NETZSCH STA 449 F1 Jupiter® instrument was given in our previous work [31]. 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 [31]. Pt/Rh (80/20) and Al_2O_3 (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 (Appendix D, see Tables D1 to D9).

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 CO_{2(g)}.

A flow rate of 70 ml/min Ar was used as the shielding gas for all runs performed in the (K₂SO₄ + K₂MoO₄), (Na₂CrO₄ + Na₂MoO₄), (K₂CrO₄ + K₂MoO₄) and (Na₂MoO₄ + K₂MoO₄) binary sub-systems. Finally, the (Na₂SO₄ + Na₂MoO₄) and (K₂SO₄ + K₂MoO₄) 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 [31]. 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 [238].

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 D9 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 Na_2MoO_4 and K_2MoO_4 were mechanically mixed at the stoichiometric composition of (35 mol% Na_2MoO_4 + 65 mol% K_2MoO_4). 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.

8.5.2 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 8.7, 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 $\text{K}_{1.29}\text{Na}_{0.70}\text{Mo}_{0.98}\text{O}_{3.92}$ while the original mechanical mixture had the composition $\text{K}_{1.3}\text{Na}_{0.7}\text{MoO}_4$.

SEM image spots for which the EDS analyses were conducted are presented in Figure D1 of the Supporting Information.

Table 8.7 EDS analysis results of selected spectra for the quenched molybdenum-glaserite sample with an estimated experimental error of $\pm 5\%$

Element	Spectrum 3	Spectrum 5	Spectrum 7	Average
O	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
Mo	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

8.6 Molybdate-based common-ion binary sub-systems

This section describes all MoO_4 -based and Mo_2O_7 -based common-ion binary sub-systems for which thermodynamic data (mainly phase equilibria) were available. Calculation of the phase diagrams was made in air ($p(\text{O}_2) = 0.21 \text{ atm}$). The gas phase was assumed to be ideal, and all gaseous species were taken from the FactPS database in FactSage [42]. These were C, C_2 , C_3 , C_4 , C_5 , O, O_2 , O_3 , CO, C_2O , CO_2 , C_3O_2 , Na, Na_2 , NaO, S, S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , S_8 , CS, CS_2 , SO, SO_2 , SO_3 , SSO, COS, Na_2SO_4 , Cl, Cl_2 , CCl, C_2Cl , CCl_2 , C_2Cl_2 , CCl_3 , C_2Cl_3 , CCl_4 , C_2Cl_4 , C_2Cl_5 , C_2Cl_6 , C_6Cl_6 , ClO, ClO_2 , ClO_3 , Cl_2O , ClOOCl , ClOClO , ClClOO , COCl, COCl_2 , NaCl, $(\text{NaCl})_2$, SCl, S_2Cl , SCl_2 , ClSSCl , SOCl_2 , SO_2Cl_2 , K, K_2 , KO, K_2SO_4 , KCl, $(\text{KCl})_2$, Cr, CrO, CrO_2 , CrO_3 , CrS, CrCl, CrCl_2 , CrCl_3 , CrCl_4 , CrCl_5 , CrCl_6 , CrOCl, CrO_2Cl , CrOCl_2 , CrO_2Cl_2 , CrOCl_3 , CrOCl_4 , Mo, Mo_2 , MoO, MoO_2 , MoO_3 , Mo_2O_6 , Mo_3O_9 , Mo_4O_{12} , Mo_5O_{15} , $\text{Mo}(\text{CO})_6$, MoCl_4 , MoCl_5 , MoCl_6 , and MoO_2Cl_2 .

The possible reactions $2 \text{A}_2\text{MO}_4 = \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$ (where A = Na, K and M = Mo, Cr) were taken into account in the calculated phase diagrams for all MO_4 -based binary sub-systems. However, those reactions were shown to be very limited up to temperatures above the liquidus [34].

8.6.1 The (NaCl + Na₂MoO₄) system

The phase diagram has been measured by Bukhalova and Mateiko [155] using the visual-polythermal 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 Mateiko [155] 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 77.5 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(s)} = Na₃ClMoO_{4(s)}] equal to zero. Then, $\Delta H_{298.15\text{ K}}^\circ$ and $S_{298.15\text{ K}}^\circ$ were adjusted to best reproduce the measured eutectic temperatures and temperature of fusion [155], while ensuring that the compound was calculated to remain stable at room temperature. The optimized thermodynamic properties ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$, and C_P) of solid Na₃ClMoO₄ are given in Table 8.2; 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 ($p(\text{O}_2) = 0.21\text{ atm}$) is shown along with the measurements in Figure 8.1.

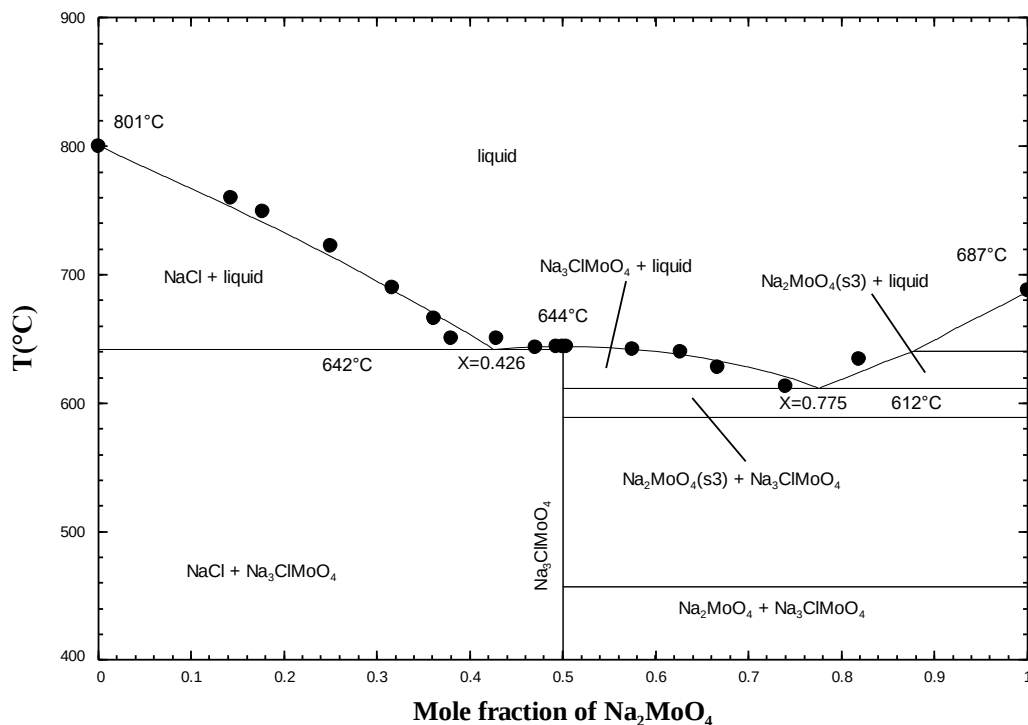


Figure 8.1 Calculated ($\text{NaCl} + \text{Na}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Bukhalova and Mateiko [155] (●)

8.6.2 The ($\text{KCl} + \text{K}_2\text{MoO}_4$) system

The phase diagram has been measured using the visual-polythermal method [155]. According to Bukhalova and Mateiko [155], ($\text{KCl} + \text{K}_2\text{MoO}_4$) is a simple eutectic system with no reported solid solutions or intermediate compounds. These authors reported a eutectic at 36.9 mol% K_2MoO_4 and 622°C. The calculated characteristics of the eutectic are 36.1 mol% K_2MoO_4 and 623°C.

The calculated ($\text{KCl} + \text{K}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 8.2.

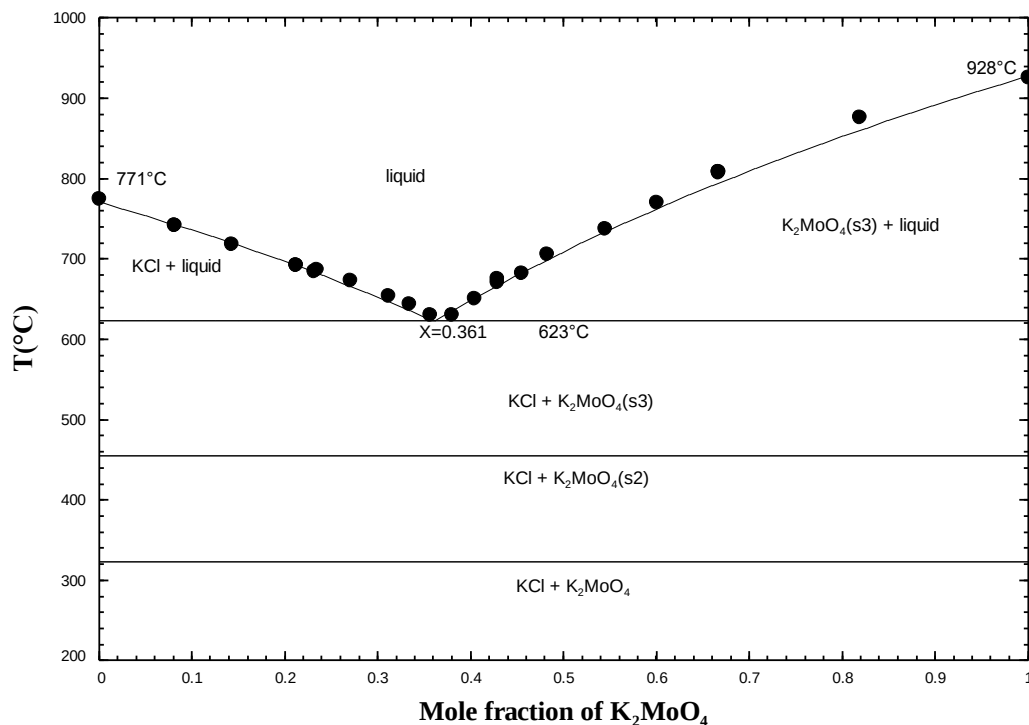


Figure 8.2 Calculated (KCl + K₂MoO₄) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Bukhalova and Mateiko [155] (●)

8.6.3 The (Na₂CO₃ + Na₂MoO₄) system

The phase diagram has been measured by Shurdumov et al [157] 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 66.6 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 $x(\text{Na}_2\text{CO}_3) = 1$ and $x(\text{Na}_2\text{MoO}_4) = 1$ respect the limiting liquidus slope equation (8.11), which assumes no solid solubility :

$$\left(\frac{dT}{dx_m^{\text{liquidus}}} \right) = \frac{RT_{\text{fusion}(m)}^2}{\Delta h_{\text{fusion}(m)}^\circ} \text{ at } [x_m = 1] \quad (8.11)$$

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 8.1). 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 Na_2MoO_4 , in the absence or presence of $\text{CO}_2(\text{g})$: 2.5, 12.7, 22, 90 and 95 mol% (from 300 to 860°C, and in the absence of $\text{CO}_2(\text{g})$); 22 mol% (from 300 to 830°C, and in the presence of $\text{CO}_2(\text{g})$); and 50 and 85 mol% (from 300 to 700°C, and in the presence of $\text{CO}_2(\text{g})$). As an example, the DSC thermogram for the binary composition (78 mol% Na_2CO_3 + 22 mol% Na_2MoO_4) in the presence of $\text{CO}_2(\text{g})$ is displayed in Figure 8.3.

The calculated (Na_2CO_3 + Na_2MoO_4) phase diagram in air ($p(\text{O}_2) = 0.21$ atm) is shown along with the experimental data in Figure 8.4. As seen in this figure, our experimental thermal arrests agree satisfactorily with the solid-solid transitions $\text{Na}_2\text{MoO}_{4(\text{S}1)} = \text{Na}_2\text{MoO}_{4(\text{S}2)}$ [31], $\text{Na}_2\text{CO}_{3(\text{S}2)} = \text{Na}_2\text{CO}_{3(\text{S}3)}$ [40], and $\text{Na}_2\text{MoO}_{4(\text{S}3)} = \text{Na}_2\text{MoO}_{4(\text{S}4)}$ [31]. Our measured liquidus temperatures in the presence of $\text{CO}_2(\text{g})$ at 22, 50 and 85 mol% Na_2MoO_4 are in excellent agreement with the data of Shurdumov et al [157]. At 22 mol% Na_2MoO_4 , our measured liquidus temperatures were about 787°C and 768°C, respectively, in the presence and absence of $\text{CO}_2(\text{g})$. This temperature shift of about 19°C is believed to be mainly attributed to the partial dissociation of $\text{Na}_2\text{CO}_{3(\text{S}3)}$ to form liquid Na_2O (dissolved in the molten salt phase) and $\text{CO}_2(\text{g})$. The calculated isobar at 1 atm is displayed in Figure 8.4, and shows that such a dissociation occurs. However, it is calculated to be extremely limited (mole fraction of Na_2O of the order of 10^{-8}). The calculated liquidus temperature of the (78 mol% Na_2CO_3 + 22 mol% Na_2MoO_4) binary mixture is 779°C, and becomes about 775°C if 1 mol% of Na_2CO_3 decomposes into Na_2O (dissolved in the liquid) and $\text{CO}_2(\text{g})$. This calculated decrease in temperature is consistent with the trend observed experimentally. When a $\text{CO}_2(\text{g})$ saturated atmosphere was used in our DSC-TGA experiments, such a decomposition was avoided.

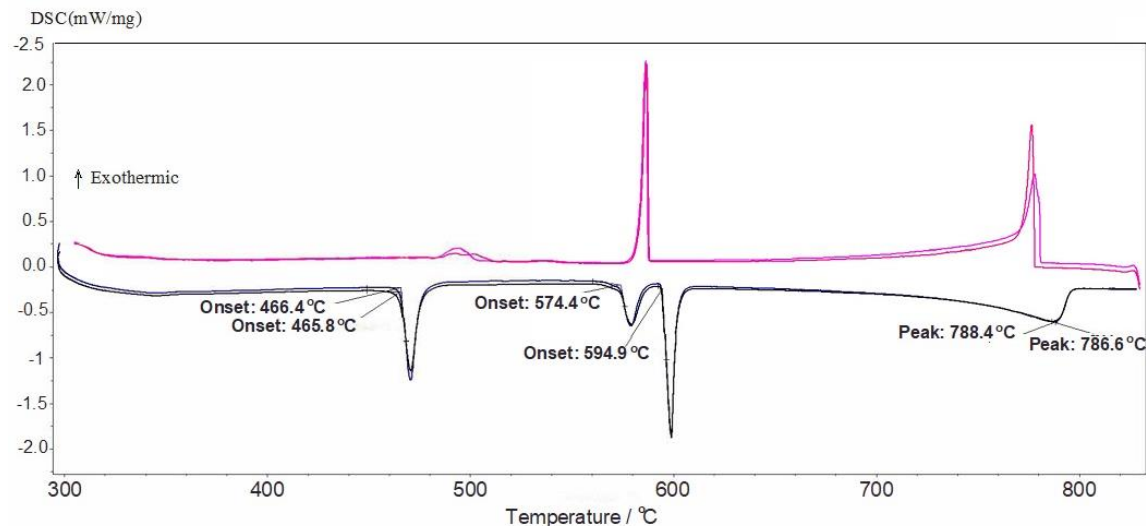


Figure 8.3 DSC thermogram for the mixture (78 mol% Na_2CO_3 + 22 mol% Na_2MoO_4) in the presence of $\text{CO}_2(\text{g})$ (2nd and 3rd heating/cooling cycles only)

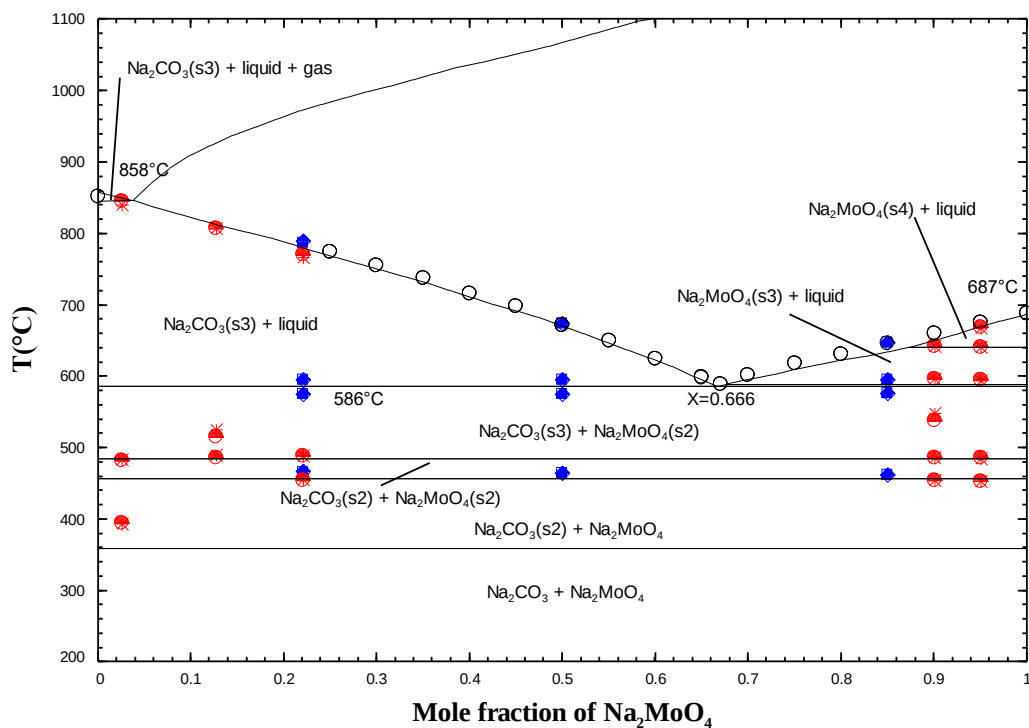


Figure 8.4 Calculated (Na_2CO_3 + Na_2MoO_4) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Shurdumov et al [157] (○) and this work (red and blue symbols) (DSC, red ● : 2nd heating without $\text{CO}_2(\text{g})$, blue ■ : 2nd heating with $\text{CO}_2(\text{g})$, red ✱ : 3rd heating without $\text{CO}_2(\text{g})$, blue ◆ : 3rd heating with $\text{CO}_2(\text{g})$)

8.6.4 The ($\text{K}_2\text{CO}_3 + \text{K}_2\text{MoO}_4$) system

The phase diagram has been investigated by Shurdumov et al [157] using thermal analysis. A eutectic was reported by these authors at 41.0 mol% K_2MoO_4 and 728°C. The calculated characteristics of the eutectic are 41.1 mol% K_2MoO_4 and 727°C. No solid solutions or intermediate compounds were reported. The measured limiting slope of the K_2MoO_4 liquidus curve agrees with equation (8.11), which shows that there is negligible solid solubility of K_2CO_3 in the high-temperature allotrope $\text{K}_2\text{MoO}_{4(\text{S}3)}$. Since no phase diagram measurements are available for K_2CO_3 -rich binary mixtures, it is not known if K_2MoO_4 is partly soluble in the high-temperature allotrope $\text{K}_2\text{CO}_{3(\text{S}2)}$, which is present as an “end-member” in the hexagonal hP22 solid solution. By analogy with the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{MoO}_4$) 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 8.5). Note that K_2MoO_4 was introduced as an “end-member” in the latter model in order to reproduce its experimental solubilities in $\text{K}_2\text{SO}_{4(\text{S}2)}$, $\text{K}_2\text{CrO}_{4(\text{S}2)}$ and $\text{Na}_2\text{MoO}_{4(\text{S}4)}$ (which are all hexagonal with the $\text{P}6_3/\text{mmc}$ space group), as will be discussed later in the sections devoted to the ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$), ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{MoO}_4$) and ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$) 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 K_2CO_3 in $\text{K}_2\text{MoO}_{4(\text{S}2)}$ (see Table 8.5).

The calculated ($\text{K}_2\text{CO}_3 + \text{K}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 8.5. According to the calculated isobar at 1 atm shown in this figure, $\text{K}_2\text{CO}_{3(\text{S}2)}$ partly decomposes into liquid K_2O (dissolved in the liquid solution) and $\text{CO}_2(\text{g})$. Nevertheless, this decomposition is calculated to be extremely limited (mole fraction of K_2O of the order of 10^{-10}).

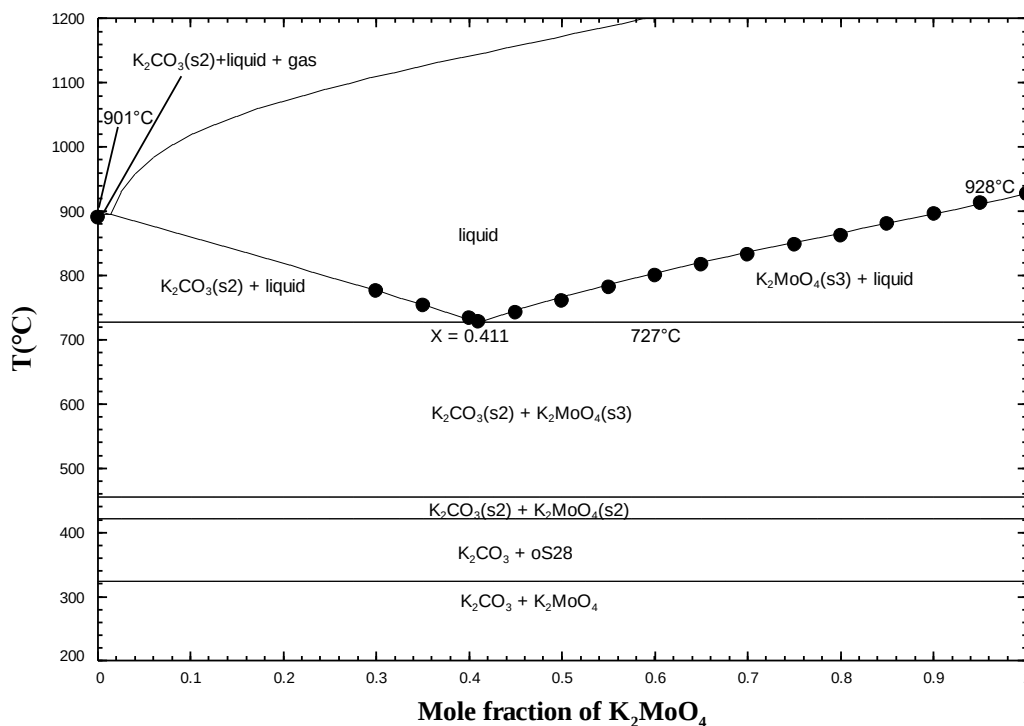


Figure 8.5 Calculated ($\text{K}_2\text{CO}_3 + \text{K}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Shurdumov et al [157] (●)

8.6.5 The ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$) system

The phase diagram has been measured by the method of cooling curves with visual readings and optical observations [107], and by the visual-polythermal method [121, 265].

A complete solid solution at high temperatures exhibiting a minimum at about 70 mol% Na_2MoO_4 was reported by Boeke [107]. Belyaev and Doroshenko [265], and Mateiko and Bukhalova [121] also observed the existence of a complete solid solution with a minimum at 75 mol% Na_2MoO_4 and 673°C, and at 70 mol% Na_2MoO_4 and 672°C, respectively.

The data of Boeke [107] suggest in particular a small solubility of Na_2SO_4 in the low-temperature allotrope $\text{Na}_2\text{MoO}_{4(\text{s}1)}$ (see Figure 8.7(a)). In this work, DSC-TGA measurements were conducted for several binary mixtures with very high concentrations of Na_2MoO_4 : 90, 92, 95, 98, and 99 mol% (from 120 to 730°C). As an example, the DSC thermogram for the binary composition (5 mol% $\text{Na}_2\text{SO}_4 + 95 \text{ mol% } \text{Na}_2\text{MoO}_4$) is shown in Figure 8.6.

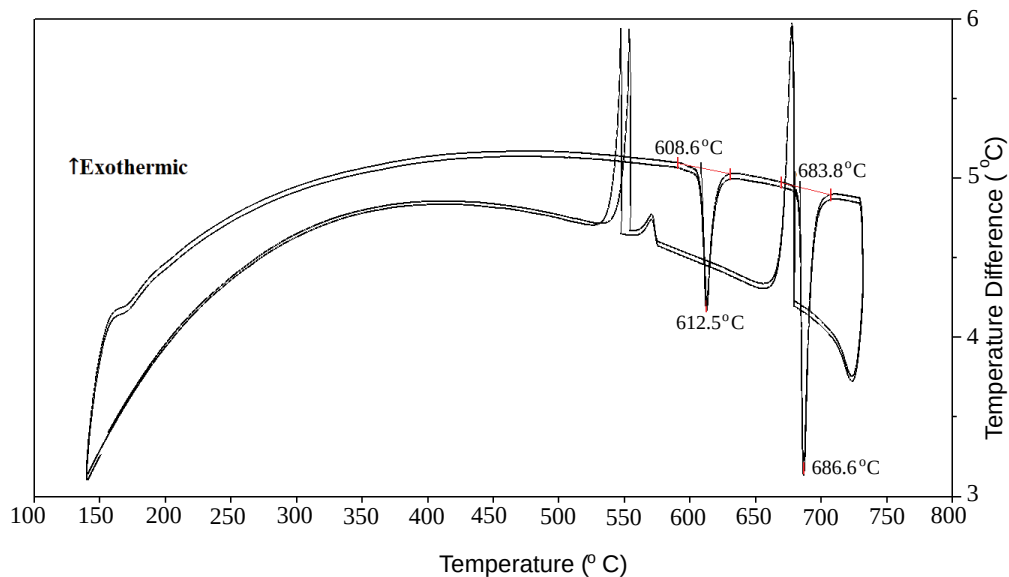


Figure 8.6 DSC thermogram for the mixture (5 mol% Na_2SO_4 + 95 mol% Na_2MoO_4) (2nd and 3rd heating/cooling cycles only)

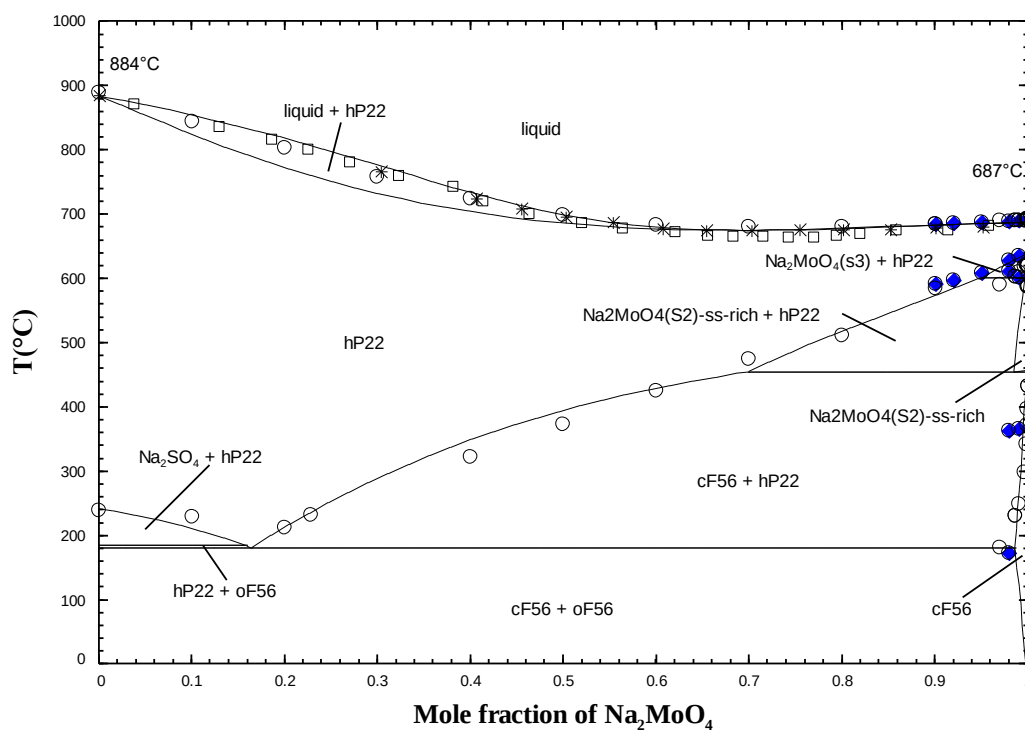


Figure 8.7(a) Calculated (Na_2SO_4 + Na_2MoO_4) phase diagram in air ($p(\text{O}_2) = 0.21$ atm). Experimental data from Boeke [107] (○), Belyaev and Doroshenko [265] (□), Mateiko and Bukhalova [121] (*) and this work (blue symbols) (DSC, ◆ : average of temperatures from 2nd and 3rd heating runs)

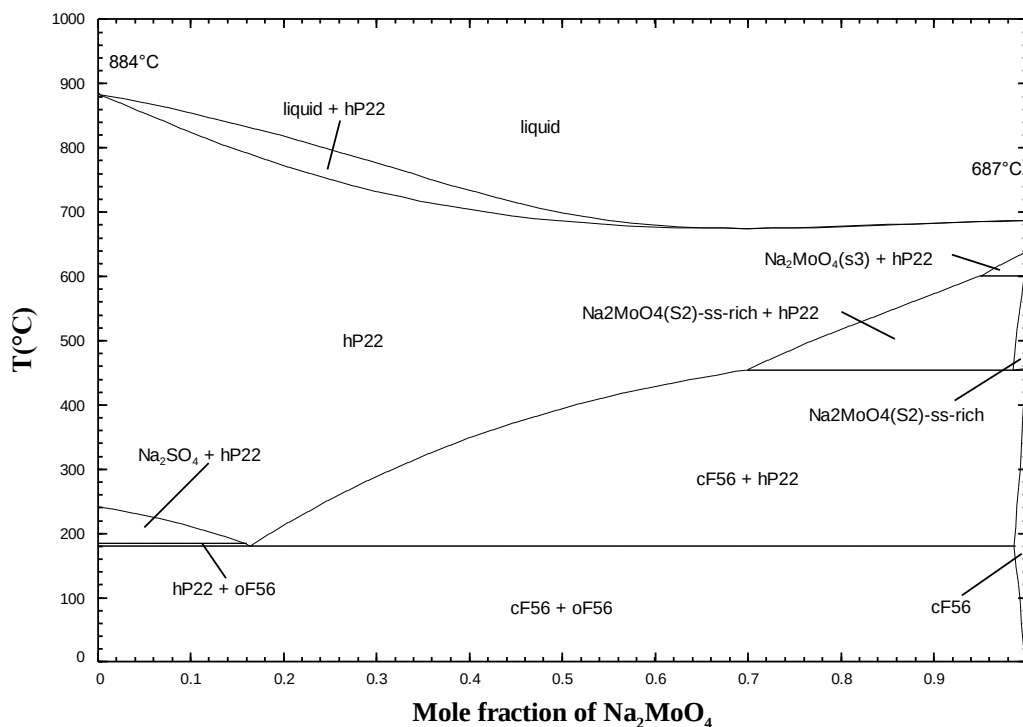


Figure 8.7(b) Calculated ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) without any experimental data

The calculated ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is shown along with the measurements in Figure 8.7(a). For the sake of clarity, the same calculated phase diagram is displayed without any experimental data in Figure 8.7(b).

The high-temperature allotropes $\text{Na}_2\text{SO}_{4(\text{S}2)}$ and $\text{Na}_2\text{MoO}_{4(\text{S}4)}$ have the same hexagonal crystal structure and space group $\text{P6}_3/\text{mmc}$ (see Table 8.1), and therefore a high-temperature solid solution (hP22) was modeled over the entire composition range. Three interaction parameters (see Table 8.5) were introduced to best reproduce the experimental data of Boeke [107] at intermediate temperatures. Then, the liquid solution was modeled in order to reproduce our experimental high-temperature data and those of [107, 121, 265]. No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the liquid phase. As seen in Table 8.4, 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 Na_2SO_4 and Na_2MoO_4)

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 SO_4^{2-} and 2.33 Å for MoO_4^{2-} [243]). The SO_4^{2-} and MoO_4^{2-} 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 [107] at low temperatures, some solid solubility of Na_2SO_4 was introduced in $\text{Na}_2\text{MoO}_{4(\text{S}1)}$ (see the cF56 solid solution in Table 8.5). By analogy with the ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) binary system (discussed later) for which Na_2CrO_4 is partly soluble in $\text{Na}_2\text{MoO}_{4(\text{S}2)}$, some solid solubility of Na_2SO_4 was also introduced in $\text{Na}_2\text{MoO}_{4(\text{S}2)}$ (see the $\text{Na}_2\text{MoO}_{4(\text{S}2)}$ -ss-rich solid solution in Table 8.5). $\text{Na}_2\text{SO}_{4(\text{S}2)}$ and $\text{Na}_2\text{CrO}_{4(\text{S}2)}$ have the same crystal structure and space group (see Table 8.1). Therefore, the Gibbs energy of the “end-member” Na_2SO_4 in the $\text{Na}_2\text{MoO}_{4(\text{S}2)}$ -ss-rich solid solution was that of $\text{Na}_2\text{SO}_{4(\text{S}2)}$ augmented by a positive Gibbs energy identical to that for the “end-member” Na_2CrO_4 . The latter model parameter was obtained from reproduction of the available phase diagram data in ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$). Finally, a regular parameter of +100,000.0 J/mol was introduced in the oS28 solid solution to calculate a negligible solid solubility of Na_2MoO_4 in $\text{Na}_2\text{SO}_{4(\text{S}1)}$, and also in the oF56 solid solution to calculate negligible mutual solubility between $\text{Na}_2\text{MoO}_{4(\text{S}3)}$ and $\text{Na}_2\text{SO}_{4(\text{S}3)}$ (see Table 8.5).

8.6.6 The ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$) system

The phase diagram has been measured by the method of cooling curves with visual readings [246], and by the visual-polythermal method [266, 267]. Amadori [246] reported a complete solid solution at high temperatures with a very flat minimum at about 6°C below the melting temperature of K_2MoO_4 (that is, at about 920°C). Similarly, Bergman et al [266], and Mateiko and Bukhalova [267] observed the formation of a complete solid solution with no marked minimum.

According to Amadori [246], it was difficult to measure the thermal arrests at around 450°C, and between 50 and 90 mol% K_2MoO_4 . This author suggested that K_2SO_4 and K_2MoO_4 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 8.8.

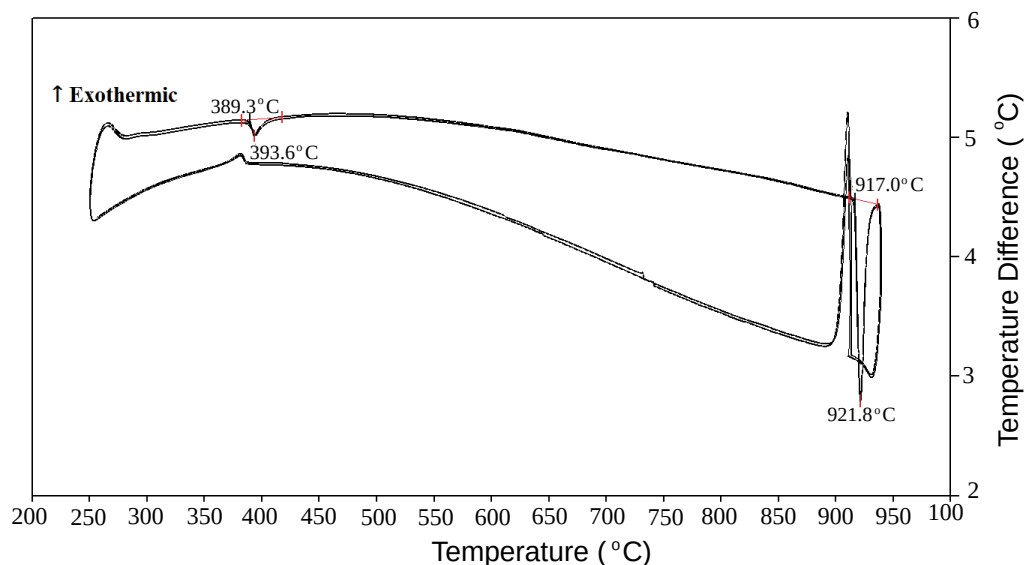


Figure 8.8 DSC thermogram for the mixture (30 mol% K_2SO_4 + 70 mol% K_2MoO_4) (2nd and 3rd heating/cooling cycles only)

The calculated (K_2SO_4 + K_2MoO_4) phase diagram in air ($p(\text{O}_2) = 0.21$ atm) is compared to the measurements in Figure 8.9. This phase diagram displays four different solid solutions : a high-temperature hexagonal solid solution (hP22) rich in $\text{K}_2\text{SO}_{4(\text{S}2)}$ and existing over a large composition range, a high-temperature trigonal solid solution ($\text{K}_2\text{MoO}_{4(\text{S}3)}$ -ht-ss) rich in $\text{K}_2\text{MoO}_{4(\text{S}3)}$ and diluted in K_2SO_4 , an orthorhombic low-temperature solid solution (oP28) rich in $\text{K}_2\text{SO}_{4(\text{S}1)}$ and diluted in K_2MoO_4 , and an orthorhombic low-temperature solid solution (oS28) rich in $\text{K}_2\text{MoO}_{4(\text{S}2)}$ and diluted in K_2SO_4 . The high-temperature allotropes $\text{K}_2\text{SO}_{4(\text{S}2)}$ (hexagonal, $\text{P6}_3/\text{mmc}$) and $\text{K}_2\text{MoO}_{4(\text{S}3)}$ (trigonal, $\text{P}\bar{3}\text{m}1$) do not have the same crystal structure (see Table 8.1). Therefore, two terminal solid solutions (hP22 and $\text{K}_2\text{MoO}_{4(\text{S}3)}$ -ht-ss) were introduced at high temperatures. The hP22 solid solution was first modelled to best reproduce the low-temperature data of Amadori

[246]; two interaction parameters were required (see Table 8.5). Simultaneously, some solubility of K_2MoO_4 in $\text{K}_2\text{SO}_{4(\text{S1})}$ (oP28 solid solution) was introduced in order to improve the agreement between our calculations and the corresponding measurements [246] for K_2SO_4 -rich mixtures. Note that $\text{K}_2\text{SO}_{4(\text{S1})}$ and $\text{K}_2\text{CrO}_{4(\text{S1})}$ 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 ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$) and ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{MoO}_4$) experimental phase diagrams. (The latter system will be discussed later). Once the hP22 solid solution was optimized, the ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$) liquid was modeled in order to best reproduce the high-temperature measurements. The $\text{K}_2\text{MoO}_{4(\text{S3})}$ -ht-ss solid solution was then modeled; the maximum solubility of K_2SO_4 in $\text{K}_2\text{MoO}_{4(\text{S3})}$ was arbitrarily set to about 6 mol%. Finally, some solubility of K_2SO_4 in $\text{K}_2\text{MoO}_{4(\text{S2})}$ (oS28 solid solution) was introduced to best reproduce the low-temperature thermal arrest of Amadori [246] 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 [39] upon optimization of the ($\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$) 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 8.5).

No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$) liquid phase. As seen in Table 8.4, 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 SO_4^{2-} and MoO_4^{2-} anions [243].

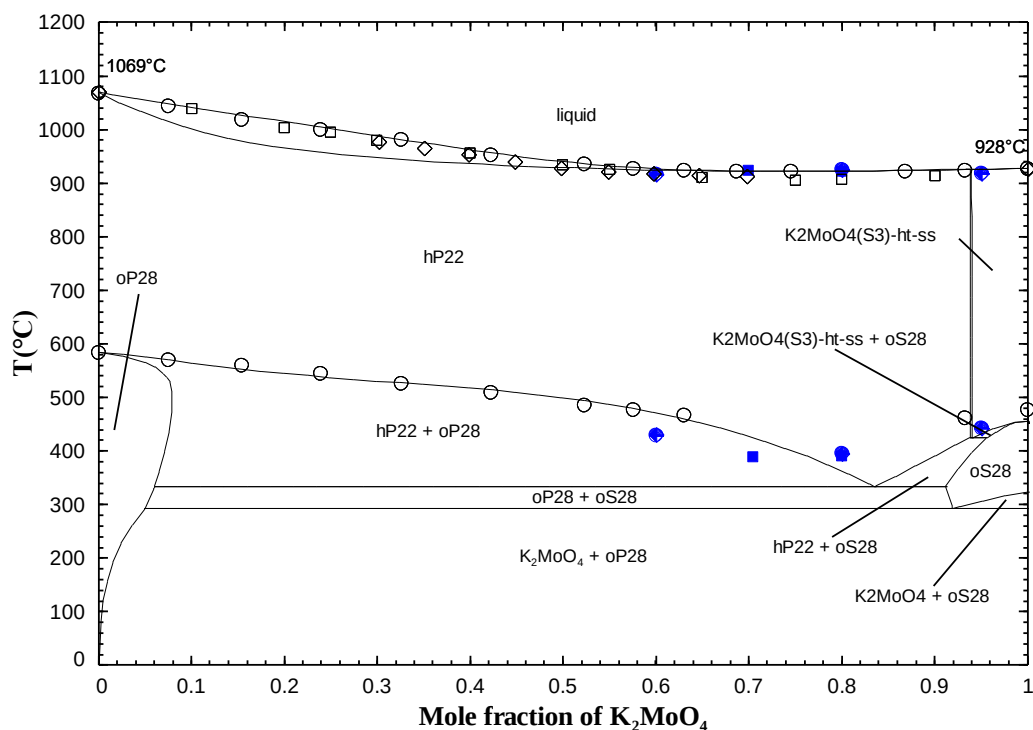


Figure 8.9 Calculated ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Amadori [246] ($\circ$), Bergman et al [266] ($\square$), Mateiko and Bukhalova [267] ($\diamond$), and this work (blue symbols) (DSC using the NETZSCH STA 449 F1 Jupiter® instrument // $\bullet$: 2nd heating, $\blacklozenge$: 3rd heating; DSC using the SDT Q600 TA Instrument // $\blacksquare$: average of temperatures from 2nd and 3rd heating runs)

8.6.7 The ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) system

The phase diagram has been measured by visual observation with a Pt/Pt-Rh thermocouple and a sensitive millivoltmeter [121]. Mateiko and Bukhalova [121] 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 mol% $\text{Na}_2\text{CrO}_4 + 90 \text{ mol% Na}_2\text{MoO}_4$) is shown in Figure 8.10.

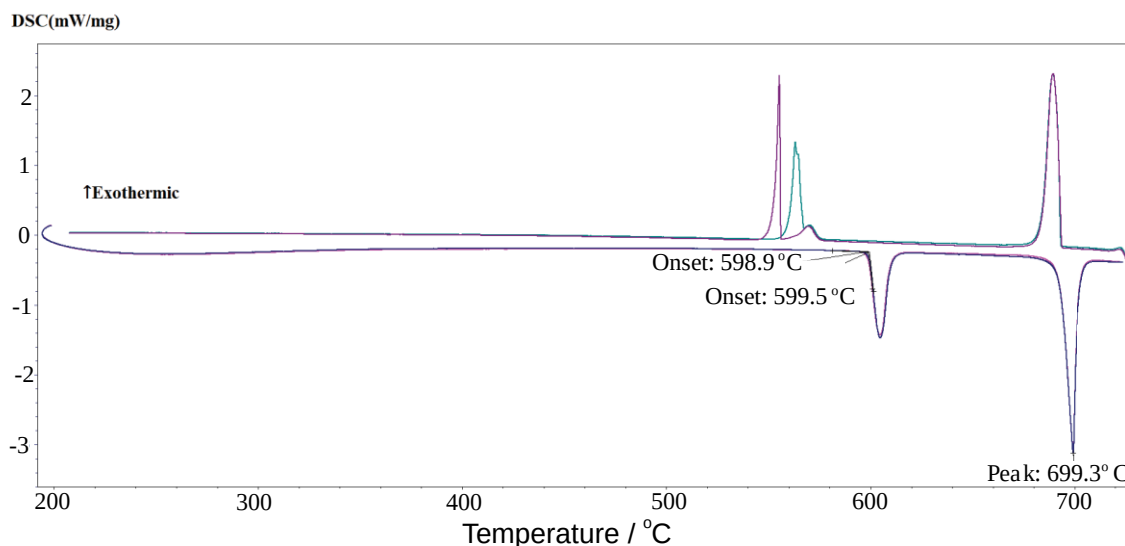


Figure 8.10 DSC thermogram for the mixture (10 mol% Na_2CrO_4 + 90 mol% Na_2MoO_4) (2nd and 3rd heating/cooling cycles only)

The calculated (Na_2CrO_4 + Na_2MoO_4) phase diagram in air ($p(\text{O}_2) = 0.21$ atm) is shown along with the measurements in Figure 8.11. 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 $\text{Na}_2\text{CrO}_{4(\text{S}2)}$ and $\text{Na}_2\text{MoO}_{4(\text{S}4)}$ are both hexagonal with the space group $\text{P6}_3/\text{mmc}$ as seen in Table 8.1), an orthorhombic low-temperature solid solution (oS28) rich in $\text{Na}_2\text{CrO}_{4(\text{S}1)}$ and diluted in Na_2MoO_4 , an intermediate-temperature orthorhombic solid solution ($\text{Na}_2\text{MoO}_{4(\text{S}2)}$ -ss-rich) rich in $\text{Na}_2\text{MoO}_{4(\text{S}2)}$ and diluted in Na_2CrO_4 , and a cubic low-temperature solid solution (cF56) rich in $\text{Na}_2\text{MoO}_{4(\text{S}1)}$ and diluted in Na_2CrO_4 .

Those four solid solutions were modeled simultaneously to best reproduce our low-temperature DSC thermal arrests. Two positive interaction parameters were required for hP22. The Gibbs energy of the “end-member” Na_2CrO_4 in the $\text{Na}_2\text{MoO}_{4(\text{S}2)}$ -ss-rich solid solution was selected to best reproduce our DSC data at 50, 70 and 90 mol% Na_2MoO_4 . Then, by analogy with the (Na_2SO_4 + Na_2MoO_4) binary system (previously discussed) for which Na_2SO_4 is partly soluble in $\text{Na}_2\text{MoO}_{4(\text{S}1)}$, some solid solubility of Na_2CrO_4 was introduced in $\text{Na}_2\text{MoO}_{4(\text{S}1)}$ (see the cF56 solid solution in Table 8.5). $\text{Na}_2\text{SO}_{4(\text{S}1)}$ and $\text{Na}_2\text{CrO}_{4(\text{S}1)}$ have the same crystal structure and space group

(see Table 8.1). Therefore, the Gibbs energy of the “end-member” Na_2CrO_4 in the cF56 solid solution was that of $\text{Na}_2\text{CrO}_{4(\text{S}1)}$ augmented by a positive Gibbs energy identical to that for the “end-member” Na_2SO_4 , which was obtained from the low-temperature data of Boeke [107] in $(\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4)$. The oS28 solid solution was then modeled to best reproduce our low-temperature DSC measurements at 10 and 30 mol% Na_2MoO_4 . 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 8.11, the former temperature is satisfactorily reproduced by our model.

The $(\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4)$ liquid phase was modelled to best reproduce the high-temperature phase equilibria. Again, no enthalpy of mixing or activity data were available to calibrate the liquid. As seen in Table 8.4, 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 Na_2CrO_4 and Na_2MoO_4) is always positive, with a maximum value of about 0.92 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-} [243]).

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 Na_2CrO_4 in $\text{Na}_2\text{MoO}_{4(\text{S}3)}$ (see Table 8.5).

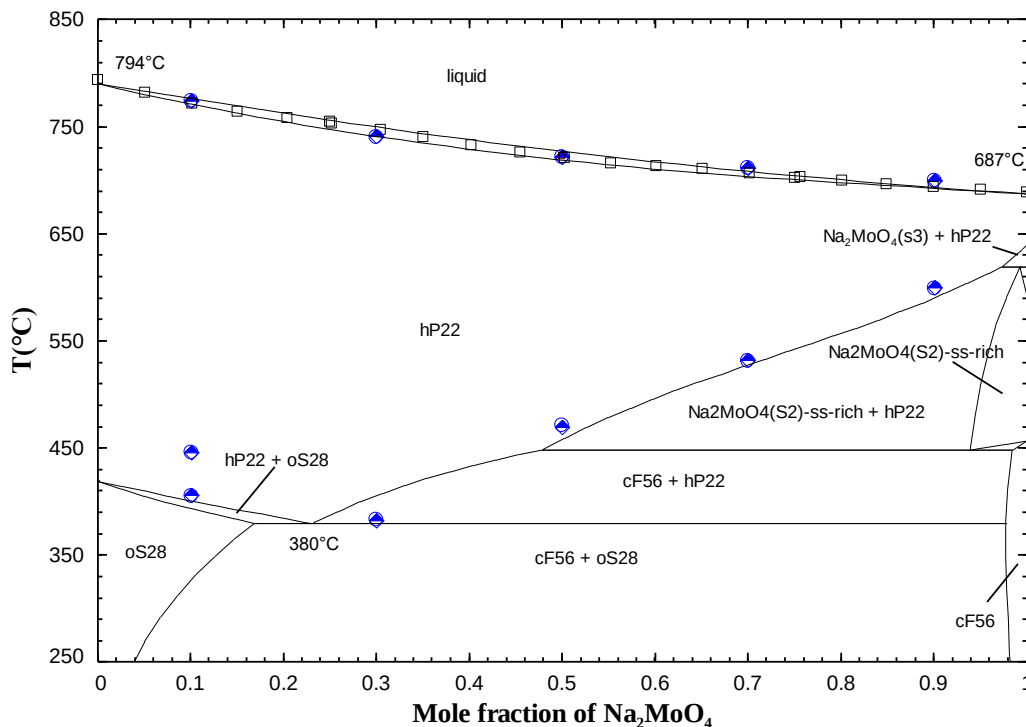


Figure 8.11 Calculated ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Mateiko and Bukhalova [121] (□) and this work (blue symbols) (DSC, blue ○ : 2nd heating, blue ◆ : 3rd heating)

8.6.8 The ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{MoO}_4$) system

The phase diagram has been measured by the method of cooling curves with visual readings [246], and the visual-polythermal method [267]. A complete solid solution was reported at high temperatures, without any marked minimum [267].

According to Amadori [246], owing to the large mutual solubility existing between K_2CrO_4 and K_2MoO_4 at 25°C, a complete solid solution is likely to exist between $\text{K}_2\text{CrO}_{4(\text{S}1)}$ and $\text{K}_2\text{MoO}_{4(\text{S}2)}$ 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 8.12.

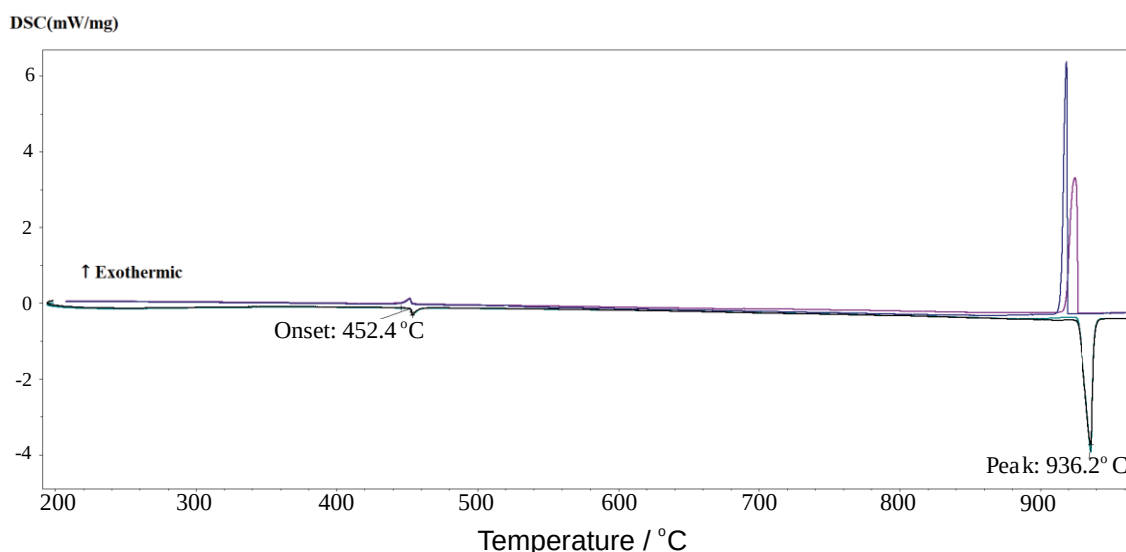


Figure 8.12 DSC thermogram for the mixture (15 mol% K_2CrO_4 + 85 mol% K_2MoO_4) (2nd and 3rd heating/cooling cycles only)

The calculated (K_2CrO_4 + K_2MoO_4) phase diagram in air ($p(\text{O}_2) = 0.21$ atm) is compared to the measurements in Figure 8.13. 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 $\text{K}_2\text{CrO}_{4(\text{S}2)}$ and existing over a large composition range, a high-temperature trigonal solid solution ($\text{K}_2\text{MoO}_{4(\text{S}3)}$ -ht-ss) rich in $\text{K}_2\text{MoO}_{4(\text{S}3)}$ and diluted in K_2CrO_4 , an orthorhombic low-temperature solid solution (oP28) rich in $\text{K}_2\text{CrO}_{4(\text{S}1)}$ and diluted in K_2MoO_4 , and an orthorhombic low-temperature solid solution (oS28) rich in $\text{K}_2\text{MoO}_{4(\text{S}2)}$ and diluted in K_2CrO_4 . Since the high-temperature allotropes $\text{K}_2\text{CrO}_{4(\text{S}2)}$ (hexagonal, $\text{P6}_3/\text{mmc}$) and $\text{K}_2\text{MoO}_{4(\text{S}3)}$ (trigonal, $\text{P}\bar{3}\text{m}1$) do not have the same crystal structure (see Table 8.1), two terminal solid solutions (hP22 and $\text{K}_2\text{MoO}_{4(\text{S}3)}$ -ht-ss) were considered at high temperatures.

The hP22 solid solution was first modelled to best reproduce the low-temperature data of Amadori [246] and our low-temperature DSC thermal arrest at 75 mol% K_2MoO_4 ; three positive interaction parameters were necessary (see Table 8.5). Some solubility of K_2MoO_4 in $\text{K}_2\text{CrO}_{4(\text{S}1)}$ (oP28 solid

solution) was introduced to improve the agreement between our calculations and the data of Amadori [246] for K_2CrO_4 -rich mixtures. As explained previously, the Gibbs energy of the “end-member” K_2MoO_4 in oP28 was obtained by optimizing simultaneously the ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{MoO}_4$) and ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$) phase diagrams. The $\text{K}_2\text{MoO}_{4(\text{S3})}$ -ht-ss solid solution was then modeled to best reproduce our low-temperature DSC thermal arrest at 85 mol% K_2MoO_4 .

Once the hP22 solid solution was optimized, the ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{MoO}_4$) 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 8.4, 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 [243].

Finally, some solubility of K_2CrO_4 in $\text{K}_2\text{MoO}_{4(\text{S2})}$ (oS28 solid solution) was introduced to best reproduce the low-temperature measurement of Amadori [246] and our low-temperature DSC thermal arrest at 95 mol% K_2MoO_4 . The Gibbs energy of the “end-member” K_2CrO_4 in the oS28 solid solution was previously selected by us [75] upon optimization of the ($\text{K}_2\text{CrO}_4 + \text{Na}_2\text{CrO}_4$) binary system ($\text{K}_2\text{MoO}_{4(\text{S2})}$ and $\text{Na}_2\text{CrO}_{4(\text{S1})}$ are mutually soluble). In this work, a very negative (-19,200.0 J/mol) constant Redlich-Kister interaction parameter had to be introduced between K_2CrO_4 and K_2MoO_4 in the oS28 solid solution (see Table 8.5).

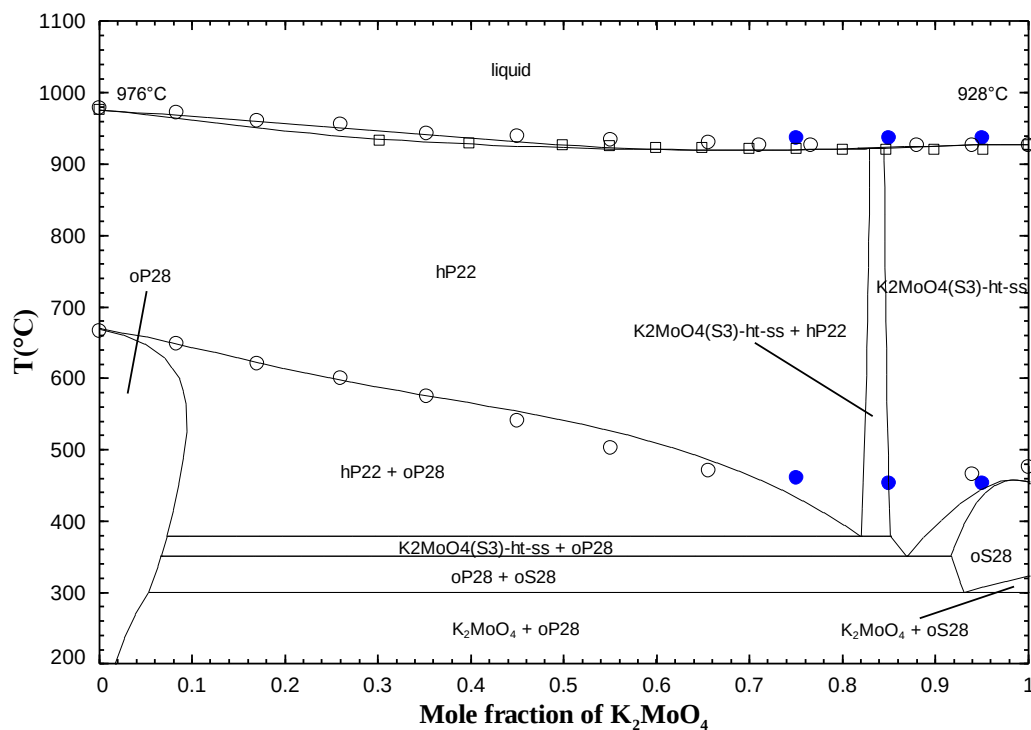


Figure 8.13 Calculated ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Amadori [246] (○), Mateiko and Bukhalova [267] (□) and this work (blue symbols) (DSC, blue ● : average of temperatures from 2nd and 3rd heating runs)

8.6.9 The ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$) system

Several studies have been performed on the ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$) binary phase diagram [155, 249, 268, 269]. Amadori [249] used the method of cooling curves with visual readings, while Belyaev and Sholokhovitch [268] 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% K_2MoO_4 and 656°C. According to Amadori [249], two terminal solid solutions (based on the high-temperature allotropes of Na_2MoO_4 and K_2MoO_4) were formed at high temperatures, and the intermediate compound $\text{Na}_2\text{MoO}_4 \cdot \text{K}_2\text{MoO}_4$ was formed upon cooling.

Using the visual-polythermal method, Bukhalova and Mateiko [155] observed a eutectic at 19 mol% K_2MoO_4 and 667°C, and also two transition points at 37 mol% K_2MoO_4 and 686°C, and at 54 mol% K_2MoO_4 and 737°C, respectively. They suggested the formation of two intermediate

compounds ($\text{Na}_2\text{MoO}_4\cdot\text{K}_2\text{MoO}_4$ and $\text{Na}_2\text{MoO}_4\cdot 2\text{K}_2\text{MoO}_4$) melting incongruently.

Din et al [269] conducted DTA and XRD measurements at both low and high temperatures. In particular, they investigated by XRD two ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$) binary mixtures at 50 and 66.7 mol% K_2MoO_4 , and the high-temperature allotropes of Na_2MoO_4 and K_2MoO_4 . They ruled out the eutectic and the two intermediate compounds reported by Bukhalova and Mateiko [155]. According to Ding et al [269], the visual-polythermal method used by Bukhalova and Mateiko to identify incongruently melting compounds cannot provide reliable results.

The calculated ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is shown along with the measurements in Figure 8.14. This phase diagram displays five different solid solutions : a high-temperature hexagonal solid solution (hP22) rich in $\text{Na}_2\text{MoO}_{4(\text{S}4)}$ and existing over a large composition range, a high-temperature trigonal solid solution ($\text{K}_2\text{MoO}_{4(\text{S}3)}$ -ht-ss) rich in $\text{K}_2\text{MoO}_{4(\text{S}3)}$ and diluted in Na_2MoO_4 , an intermediate-temperature orthorhombic solid solution (oF56) rich in $\text{Na}_2\text{MoO}_{4(\text{S}3)}$ and diluted in K_2MoO_4 , a low-temperature orthorhombic solid solution (oS28) rich in $\text{K}_2\text{MoO}_{4(\text{S}2)}$ and diluted in Na_2MoO_4 , and the non-stoichiometric phase $\text{K}_3\text{Na}(\text{MoO}_4)_2$ (molybdenum-glaserite, hP14). These various solid solutions and the optimized model parameters are described in detail in Table 8.5.

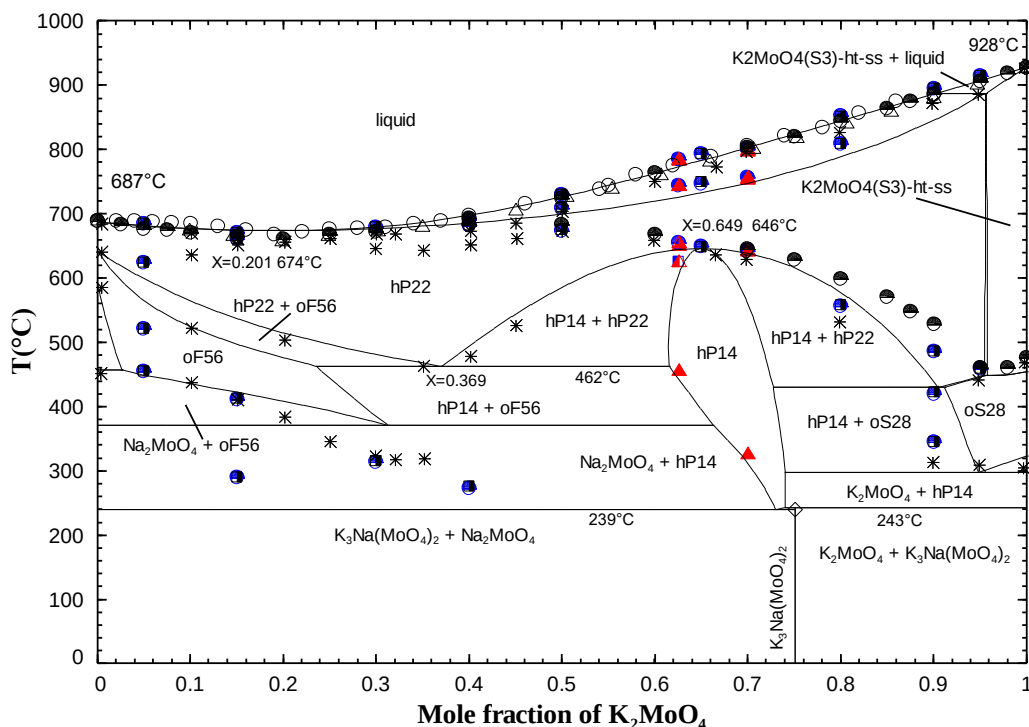


Figure 8.14 Calculated ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$).

Experimental data from Amadori [249] ($\bullet$), Belyaev and Sholokhov [268] ($\triangle$), Bukhalova and Mateiko [155] ($\circ$), Ding et al [269] ($\ast$), Fabry et al [44] ($\diamond$) and this work (red and blue symbols) (DSC, red $\blacktriangle$: 1st heating for molybdenum-glaserite equilibrated at 400°C for 4 weeks, red $\blacktriangle$: 2nd heating for molybdenum-glaserite equilibrated at 400°C for 4 weeks, red $\blacktriangle$: 3rd heating for molybdenum-glaserite equilibrated at 400°C for 4 weeks, blue $\bullet$: 2nd heating for mechanical mixtures of pre-treated reagents, blue $\blacksquare$: 3rd heating for mechanical mixtures of pre-treated reagents)

Ding et al [269] claimed that the high temperature allotropes of Na_2MoO_4 and K_2MoO_4 are isomorphic (i.e. same crystal structure and space group). However, based on our previous work [31], $\text{Na}_2\text{MoO}_{4(\text{S4})}$ (hexagonal, $P6_3/\text{mmc}$) and $\text{K}_2\text{MoO}_{4(\text{S3})}$ (trigonal, $P\bar{3}m1$) do not have the same crystal structure (see Table 8.1). Therefore, two terminal solid solutions (hP22 and $\text{K}_2\text{MoO}_{4(\text{S3})}\text{-ht-ss}$) were modeled at high temperatures in the present work.

For the molybdenum-glaserite phase $\text{K}_3\text{Na}(\text{MoO}_4)_2$, a solid-solid transition occurs at 513K [44] between a stoichiometric compound (monoclinic, space group $C2/c$), which is stable at room

temperature, and a non-stoichiometric phase (trigonal, $P\bar{3}m1$) [44, 90]. There is some similarity with cryolite (Na_3AlF_6), for which a solid-solid transition occurs at about 834K between a stoichiometric compound (monoclinic, space group $P2_1/n$) and a non-stoichiometric phase (cubic, space group $\text{Fm}\bar{3}m$) [270].

As shown in Table 8.5, the high-temperature non-stoichiometric glaserite phase (hP14) was modelled with the following sublattice structure : $(\text{K}^+, \text{Na}^+)_3(\text{Na}^+)(\text{SO}_4^{2-}, \text{CrO}_4^{2-}, \text{MoO}_4^{2-})_2$. The sulfur-glaserite [39] and chrome-glaserite [75] phases were modelled previously, and the corresponding model parameters were used directly in this work. To model the molybdenum-glaserite phase, the two new “end-members” $\text{K}_3\text{Na}(\text{MoO}_4)_2$ and $\text{Na}_3\text{Na}(\text{MoO}_4)_2$ 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 $\text{Na}_2\text{MoO}_{4(\text{S}1)} = \text{Na}_2\text{MoO}_{4(\text{S}2)}$ plus 1.5 times that for the transition $\text{K}_2\text{MoO}_{4(\text{S}1)} = \text{K}_2\text{MoO}_{4(\text{S}2)}$. Note that the temperatures and enthalpy changes for these two solid-solid transitions were directly taken from our previous study [31].

The enthalpy change for the solid-solid transition of $\text{K}_3\text{Na}(\text{MoO}_4)_2$ was estimated as 26,980.0 J/mol at 513K. The low-temperature stoichiometric compound $\text{K}_3\text{Na}(\text{MoO}_4)_2$ was introduced in this work. Its Gibbs energy was estimated by starting with a Gibbs energy of formation from the pure end-members $[0.5 \text{ Na}_2\text{MoO}_{4(\text{S}1)} + 1.5 \text{ K}_2\text{MoO}_{4(\text{S}1)} = \text{K}_3\text{Na}(\text{MoO}_4)_{2(\text{S})}]$ equal to zero. Then, $\Delta H_{298.15 \text{ K}}^\circ$ and $S_{298.15 \text{ K}}^\circ$ were adjusted to best reproduce the experimental temperature [44] and assessed enthalpy change for the solid-solid transition of molybdenum-glaserite. The reactions $0.055 \text{ Na}_2\text{MoO}_{4(\text{S}1)} + 0.945 \text{ K}_3\text{Na}(\text{MoO}_4)_{2(\text{S})} = 0.973 \text{ hP14}$ and $\text{K}_3\text{Na}(\text{MoO}_4)_{2(\text{S})} = 0.959 \text{ hP14} + 0.083 \text{ K}_2\text{MoO}_{4(\text{S}1)}$ were calculated at 239°C (enthalpy change of 26,988 J/mol) and 243°C (enthalpy change of 25,826 J/mol), respectively.

The optimized thermodynamic properties ($\Delta H_{298.15 \text{ K}}^\circ$, $S_{298.15 \text{ K}}^\circ$, and C_P) of the stoichiometric compound $\text{K}_3\text{Na}(\text{MoO}_4)_2$ are given in Table 8.2. The Open Quantum Materials Database (OQMD) [128, 129] 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 [130]

is -2,955,539 J/mol.

In this work, DSC-TGA measurements were conducted for mechanical mixtures of the pre-treated reagents Na_2MoO_4 and K_2MoO_4 . Nine different binary mixtures with various contents of K_2MoO_4 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 molybdenum-glaserite composition of (35 mol% Na_2MoO_4 + 65 mol% K_2MoO_4) equilibrated at 400°C for four weeks, to which an excess of Na_2MoO_4 or K_2MoO_4 was added subsequently. Two binary mixtures at 62.5 and 70 mol% K_2MoO_4 were studied under those conditions, from 180 to 840°C. All measured thermal arrests are listed in the Supporting Information (see Tables D8 and D9). As an example, the DSC thermogram for the mechanical mixture (70 mol% Na_2MoO_4 + 30 mol% K_2MoO_4) is displayed in Figure 8.15.

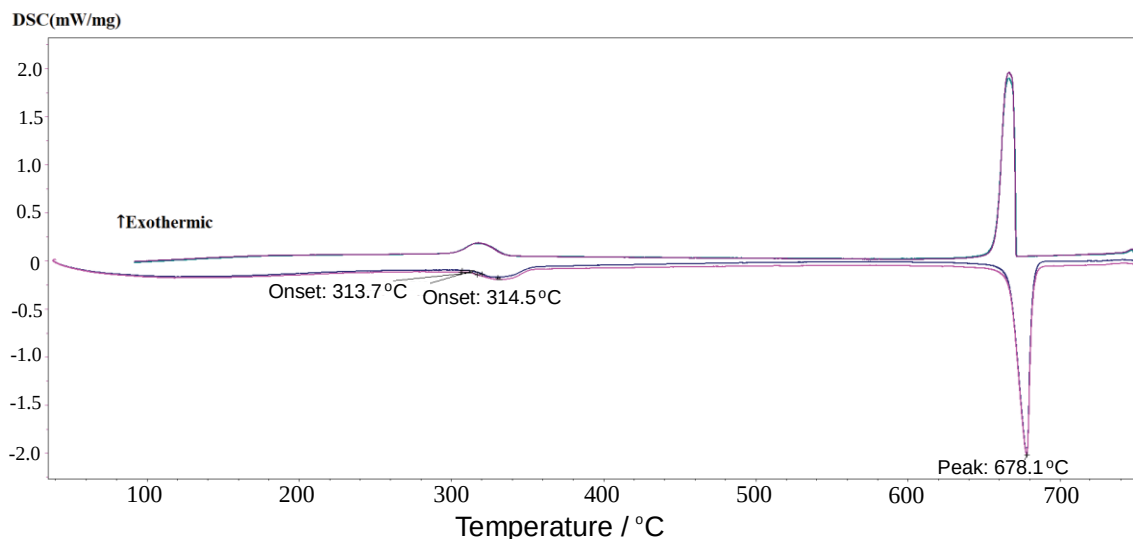


Figure 8.15 DSC thermogram for the mixture (70 mol% Na_2MoO_4 + 30 mol% K_2MoO_4) (2nd and 3rd heating/cooling cycles only)

No experimental data (such as enthalpy of mixing or activity data) were available to calibrate the (Na_2MoO_4 + K_2MoO_4) liquid phase. First, a constant parameter of -1,419.6 J/mol was used by analogy with the (Na_2SO_4 + K_2SO_4) [39] and (Na_2CrO_4 + K_2CrO_4) [75] 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 ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$) liquid (see Table 8.4). The enthalpy of mixing of the liquid calculated at 950°C (that is, above the temperatures of fusion of Na_2MoO_4 and K_2MoO_4) 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 [214].

Then, the hexagonal solid solution (hP22) was modelled in order to best reproduce the high-temperature measurements (i.e. phase equilibria with the liquid solution) and the maximum extension of the molybdenum-glaserite phase (hP14) at about 646°C and 64.9 mol% K_2MoO_4 . Only one positive model parameter was required for hP22, and the Gibbs energies of the two “end-members” $\text{K}_3\text{Na}(\text{MoO}_4)_2$ and $\text{Na}_3\text{Na}(\text{MoO}_4)_2$ in hP14 were optimized simultaneously. To model the oF56 solid solution, the data of Ding et al [269] were favoured, and four model parameters were used : two parameters (including one temperature-dependent parameter) for the Gibbs energy of the “end-member” K_2MoO_4 , and two Redlich-Kister interaction parameters. As seen in Figure 8.14, the calculated extent of oF56 is reasonable, and the eutectoid reaction $\text{hP22} = \text{oF56} + \text{hP14}$ is calculated at about 36.9 mol% K_2MoO_4 and 462°C. Finally, the $\text{K}_2\text{MoO}_{4(\text{S3})}$ -ht-ss and oS28 solid solutions were modeled to best reproduce, respectively, the high-temperature and low-temperature measurements of Amadori [249] and Ding et al [269]. The maximum solubility of Na_2MoO_4 in $\text{K}_2\text{MoO}_{4(\text{S3})}$ was arbitrarily set to about 4.3 mol%.

8.6.10 The ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Mo}_2\text{O}_7$) system

The phase diagram has been measured by Amadori [133] using the method of cooling curves with visual readings, and a complete solid solution was reported at high temperatures.

The calculated ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Mo}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 8.16.

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, $\Delta g_{\text{K}_2/(\text{Cr}_2\text{O}_7)(\text{Mo}_2\text{O}_7)} = 0$) owing to the expected similarity of the radii of the anions $\text{Cr}_2\text{O}_7^{2-}$ and $\text{Mo}_2\text{O}_7^{2-}$. As seen in Table 8.1, the high-temperature

allotropes $\text{K}_2\text{Cr}_2\text{O}_7(\text{s}_2)$ and $\text{K}_2\text{Mo}_2\text{O}_7(\text{s}_2)$ are both monoclinic with the space group $\text{P}2_1/\text{c}$. Therefore, a high-temperature solid solution ($\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s.})$) was introduced over the entire composition range. One positive regular parameter was used to reproduce the experimental solidus of Amadori [133] from 0 to about 70 mol% $\text{K}_2\text{Mo}_2\text{O}_7$. Amadori reported for $\text{K}_2\text{Mo}_2\text{O}_7$ a melting temperature about 65°C lower than our selected value, which was based on the available data from the literature [34]. Hence, it was not possible to reproduce the experimental solidus of Amadori [133] above 70 mol% $\text{K}_2\text{Mo}_2\text{O}_7$.

The low-temperature allotropes $\text{K}_2\text{Cr}_2\text{O}_7(\text{s}_1)$ and $\text{K}_2\text{Mo}_2\text{O}_7(\text{s}_1)$ are both triclinic with the space group $\text{P}\bar{1}$ (see Table 8.1). Thus, a low-temperature solid solution (aP44) was modelled 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 $\text{K}_2\text{Cr}_2\text{O}_7(\text{s.s.})$ solid solution was used.

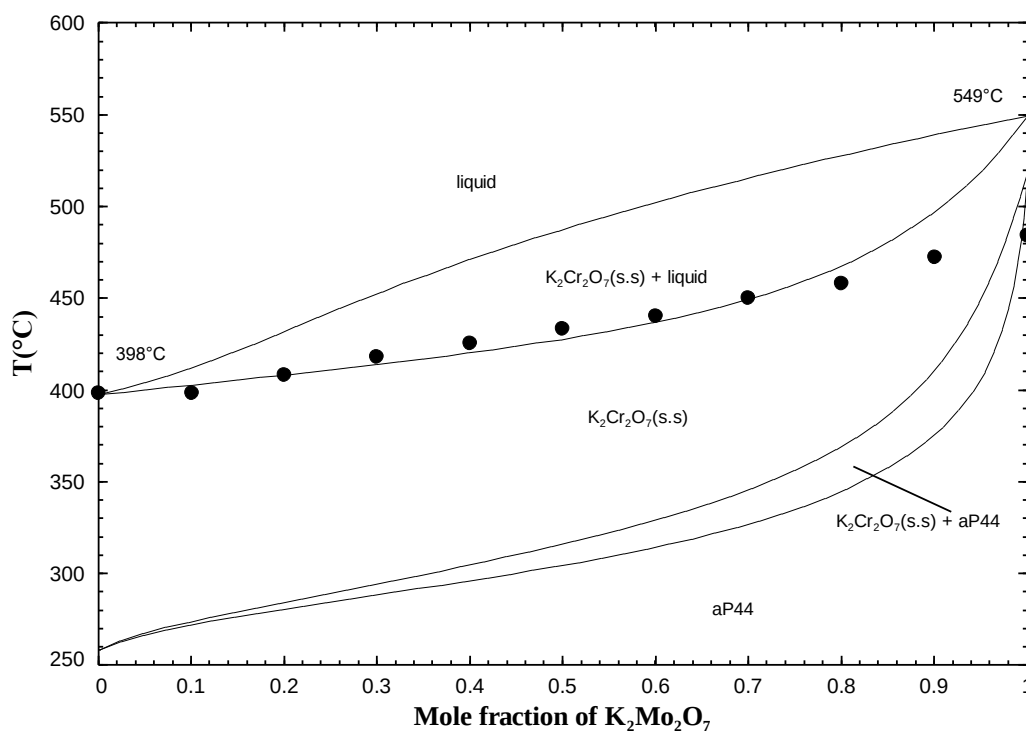


Figure 8.16 Calculated ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Mo}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$).

Experimental data from Amadori [133] (●)

8.6.11 The ($\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7$) system

The ($\text{Na}_2\text{MoO}_4 + \text{MoO}_3$) phase diagram has been measured by thermal analysis [164, 271] and DTA [151]. The relevant compositions were expressed in terms of the ($\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7$) binary sub-system. These various authors reported a eutectic at 37.0 mol% $\text{Na}_2\text{Mo}_2\text{O}_7$ and 551°C, 35.1 mol% $\text{Na}_2\text{Mo}_2\text{O}_7$ and 556°C, and 25.0 mol% $\text{Na}_2\text{Mo}_2\text{O}_7$ and 559°C, respectively. The calculated characteristics of the eutectic are 36.6 mol% $\text{Na}_2\text{Mo}_2\text{O}_7$ and 551°C. Using thermal analysis, Mokhosev and Fedorov [272] measured the ($\text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{CO}_3$) phase diagram, and claimed that “this system can be represented as two binary systems : ($\text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{MoO}_4$) and ($\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{CO}_3$)”. Measurements were provided graphically for the ($\text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{MoO}_4$) phase diagram, and a eutectic was reported at 40.0 mol% $\text{Na}_2\text{Mo}_2\text{O}_7$ and 538°C.

The calculated ($\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is shown along with the measurements in Figure 8.17. The data of Mokhosev and Fedorov [272] were discarded since it is not clear how they were obtained. Also, the corresponding experimental liquidus of $\text{Na}_2\text{Mo}_2\text{O}_7$ substantially disagrees with those of the other studies [151, 164, 271]. The measurements of Groschuff [271] were favoured in this work since, at the same time, this author obtained satisfactory data for the ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$) phase diagram [75]. As seen in Table 8.4, one of the two model parameters required for the ($\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7$) 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 Na_2MoO_4 and $\text{Na}_2\text{Mo}_2\text{O}_7$) 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.

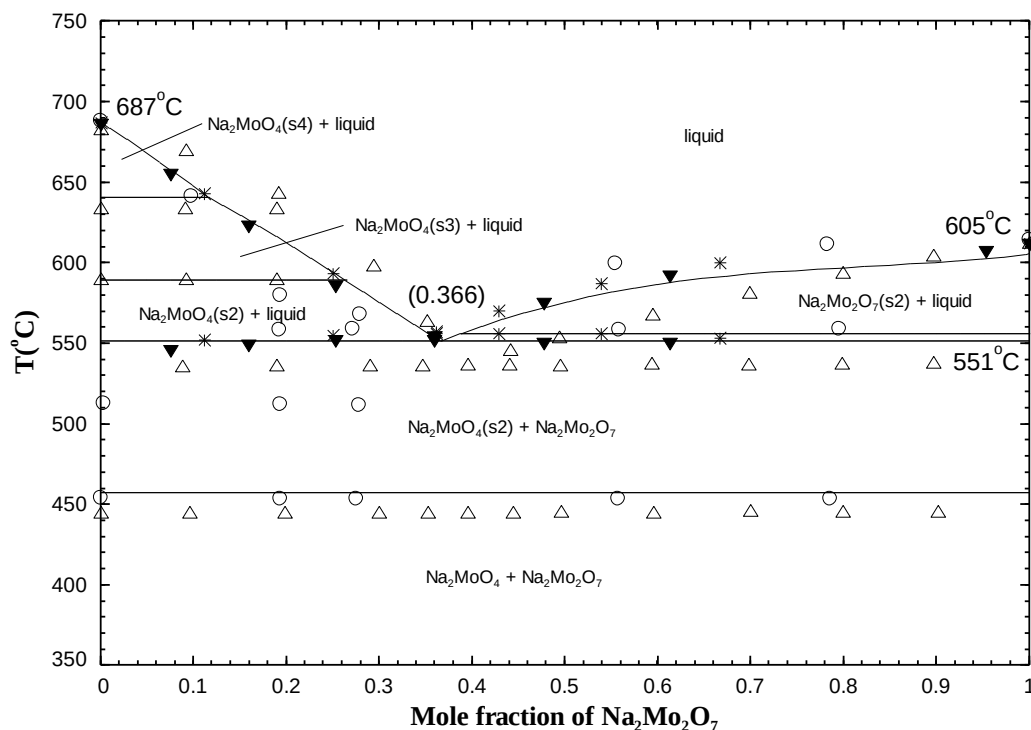


Figure 8.17 Calculated ($\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$).

Experimental data from Groschuff [271] (▼), Hoermann [164] (*), Caillet [151] (○), and Mokhosoiev and Fedorov [272] (△)

8.6.12 The ($\text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7$) system

The ($\text{K}_2\text{MoO}_4 + \text{MoO}_3$) phase diagram has been measured by thermal analysis [164, 273] and DTA [151]. The relevant compositions were expressed in terms of the ($\text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7$) binary subsystem. Amadori [273] and Caillet [151] reported a eutectic at 475–480°C, and 61.3 mol% $\text{K}_2\text{Mo}_2\text{O}_7$ and 480°C, respectively. The calculated ($\text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$) is compared to the measurements in Figure 8.18. The ($\text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7$) binary liquid was assumed to be ideal (that is, $\Delta g_{\text{K}_2/(\text{MoO}_4)(\text{Mo}_2\text{O}_7)} = 0$). Under those conditions, the experimental liquiduses of K_2MoO_4 from Amadori [273] and Hoermann [164] are satisfactorily reproduced by the model up to about 80 mol% $\text{K}_2\text{Mo}_2\text{O}_7$. However, for compositions richer in $\text{K}_2\text{Mo}_2\text{O}_7$, a large discrepancy is observed between the calculations and the available data. In particular, the calculated characteristics of the eutectic are 82.4 mol% $\text{K}_2\text{Mo}_2\text{O}_7$ and 527°C, which overestimates the reported eutectic temperature. This is due to the fact that the experimental

melting temperatures of $\text{K}_2\text{Mo}_2\text{O}_7$ from [151, 164, 273] are substantially lower than our selected value of 549°C , which was based on a critical review of the literature [34]. There is some uncertainty in our calculated ($\text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7$) phase diagram above about 80 mol% $\text{K}_2\text{Mo}_2\text{O}_7$, including our calculated eutectic temperature of 527°C .

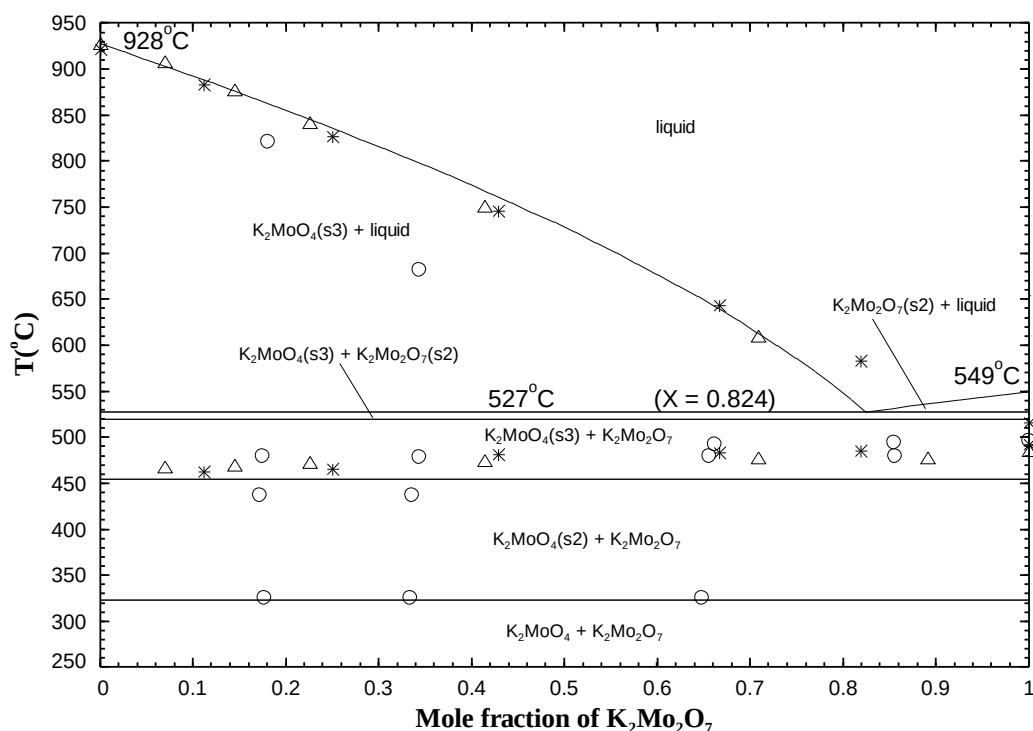


Figure 8.18 Calculated ($\text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7$) phase diagram in air ($p(\text{O}_2) = 0.21 \text{ atm}$). Experimental data from Amadori [273] ($\triangle$), Hoermann [164] ($\ast$), and Caillet [151] ($\circ$)

8.7 Molybdate-based common-cation ternary sub-systems : ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$)

To our knowledge, experimental data are available only for the ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) sub-system. The liquidus surface of this system was investigated by Mateiko and Bukhalova [121] using visual observations. Six isoplethal sections were measured. The calculated liquidus projection is shown in Figure 8.19; 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 8.20 to 8.22. The remaining three isoplethal sections are given in the Supplementary Information (see Figures D2 to D4). 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 ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$) binary sub-system was modelled previously [75], and the corresponding model parameters were used directly in this work. Measurements in Figures 8.20, 8.22, D2 and D4 agree better with the calculated liquidus whereas data in Figure 8.21 agree better with the calculated solidus. Overall, agreement between the calculations and the measurements of Mateiko and Bukhalova [121] is satisfactory.

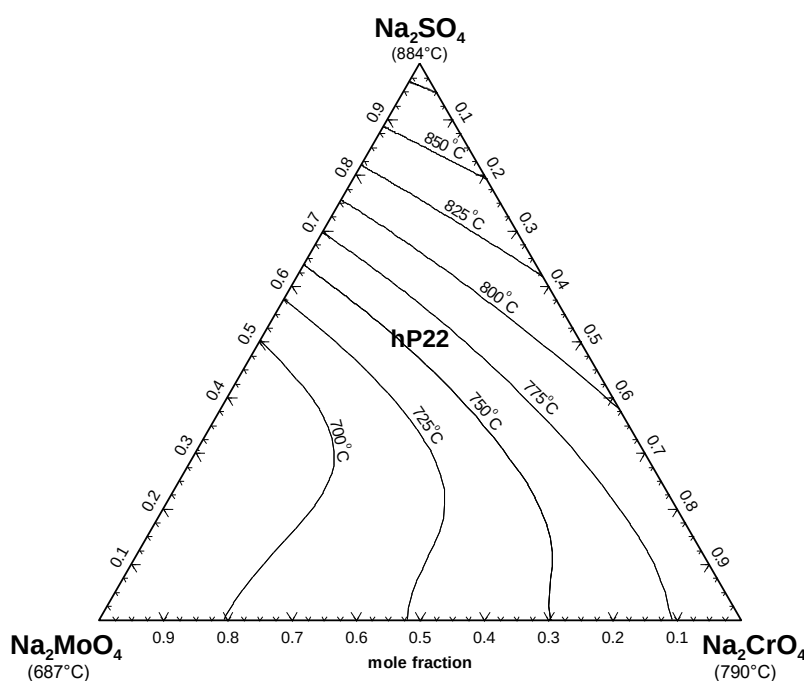


Figure 8.19 Calculated liquidus projection of the ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) system

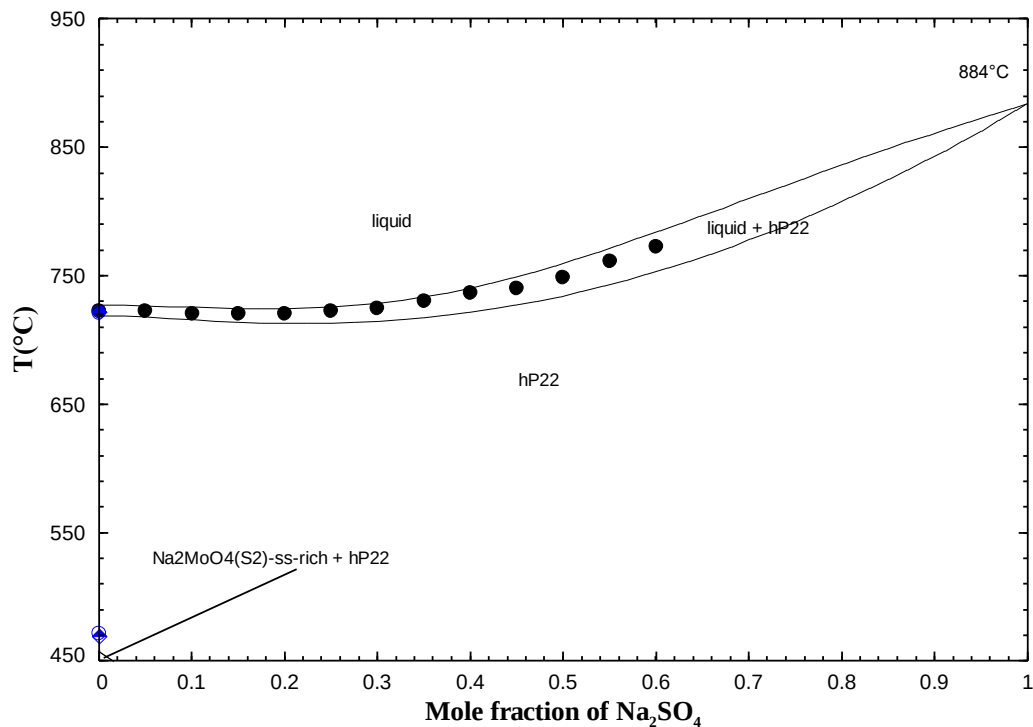


Figure 8.20 Calculated isoplethal section in the ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) system ($(\text{Na}_2\text{CrO}_4)_{0.5}(\text{Na}_2\text{MoO}_4)_{0.5}\text{-Na}_2\text{SO}_4$, section I). Experimental data from Mateiko and Bukhalova [121] (●) and this work (blue symbols) (DSC, blue ○ : 2nd heating, blue ◇ : 3rd heating)

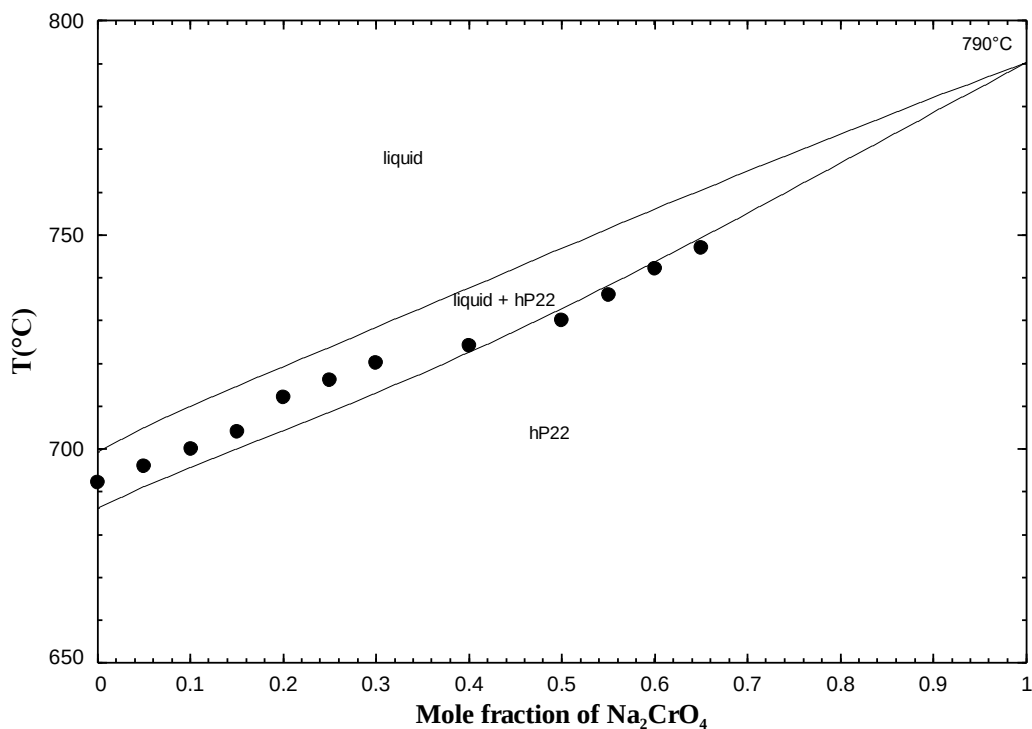


Figure 8.21 Calculated isoplethal section in the ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) system

$((\text{Na}_2\text{SO}_4)_{0.5}(\text{Na}_2\text{MoO}_4)_{0.5}-\text{Na}_2\text{CrO}_4$, section IV). Experimental data from Mateiko and Bukhalova [121] (●)

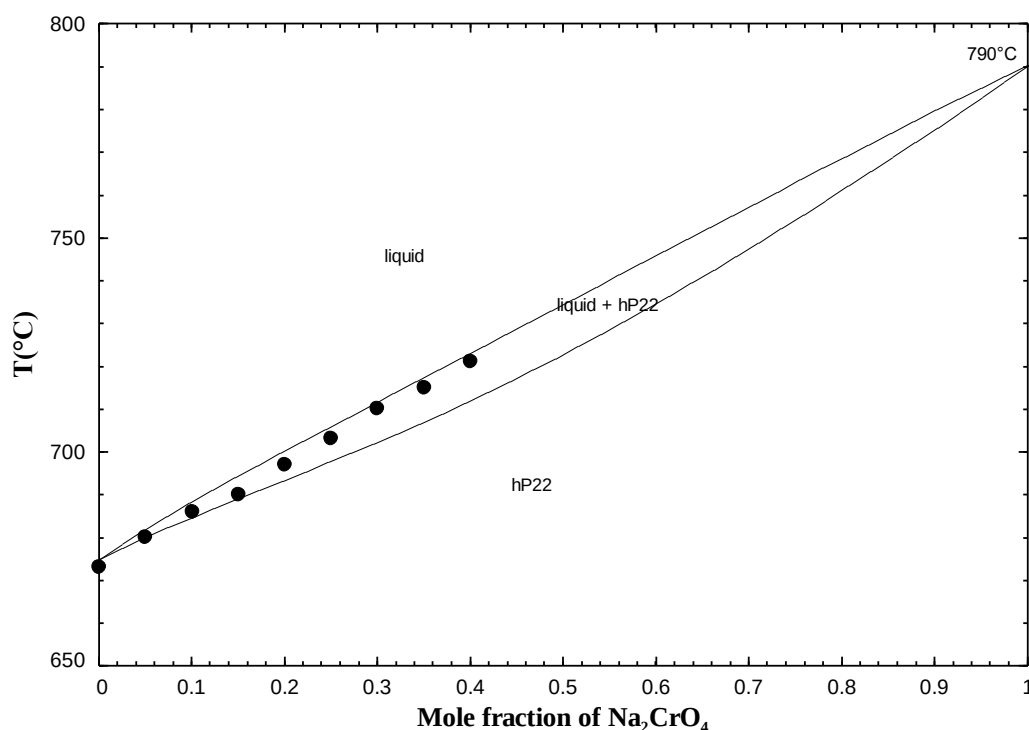


Figure 8.22 Calculated isoplethal section in the $(\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4)$ system $((\text{Na}_2\text{SO}_4)_{0.3}(\text{Na}_2\text{MoO}_4)_{0.7}-\text{Na}_2\text{CrO}_4$, section VI). Experimental data from Mateiko and Bukhalova [121] (●)

8.8 Molybdate-based ternary reciprocal sub-systems : $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4)$

To our knowledge, experimental data are available only for the $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4)$ sub-system. Seventeen isoplethal sections (including the $(\text{K}_2\text{MoO}_4 + \text{Na}_2\text{Cl}_2)$ and $(\text{Na}_2\text{MoO}_4 + \text{K}_2\text{Cl}_2)$ diagonal sections) were measured by Bukhalova and Mateiko [155] 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 8.23. In the reciprocal square in this figure, the four apices correspond to the pure salts: NaCl, KCl, Na_2MoO_4 , and K_2MoO_4 . 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 8.4). The (NaCl + KCl) common-anion binary sub-system was modelled previously [220], 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 8.24 to 8.28. The remaining twelve isoplethal sections are given in the Supplementary Information (see Figures D5 to D16). 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 [155]. Overall, agreement between the calculations and the available measurements is satisfactory.

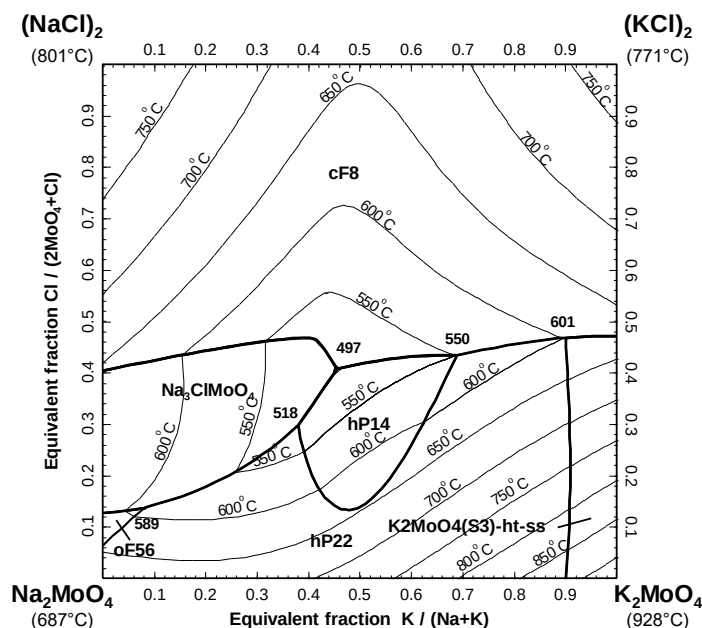


Figure 8.23 Calculated liquidus projection of the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system

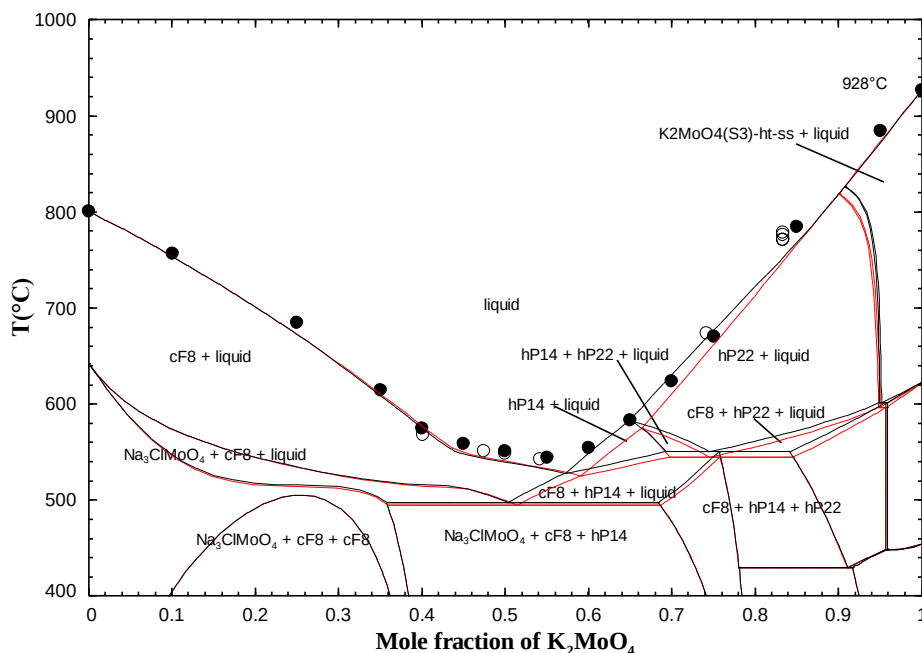


Figure 8.24 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system (Na₂Cl₂-K₂MoO₄ diagonal section). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter). Experimental data from Bukhalova and Mateiko [155] (●, ○)

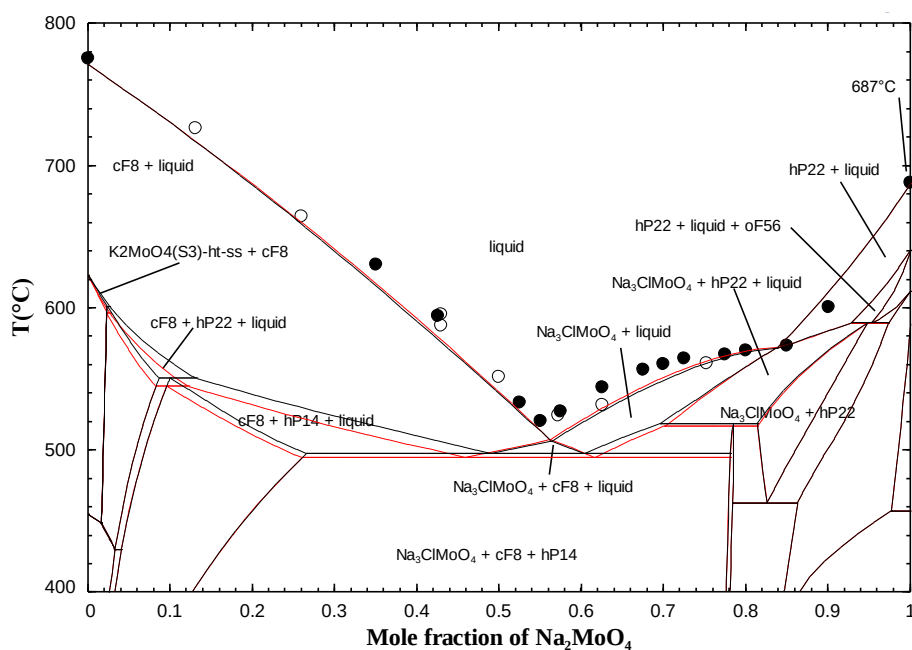


Figure 8.25 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system (K₂Cl₂-Na₂MoO₄ diagonal section). Black lines: final calculations (with one ternary reciprocal

parameter); red lines: predictions (without any ternary reciprocal parameter). Experimental data from Bukhalova and Mateiko [155](●, ○)

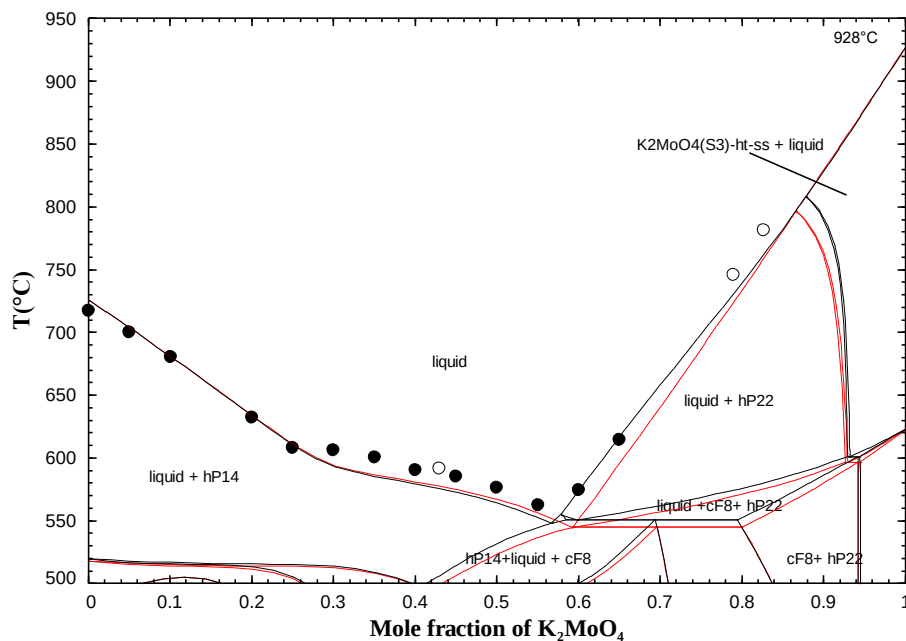


Figure 8.26 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system ((Na₂Cl₂)_{0.75}(K₂Cl₂)_{0.25}-K₂MoO₄, section I). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [155](●, ○)

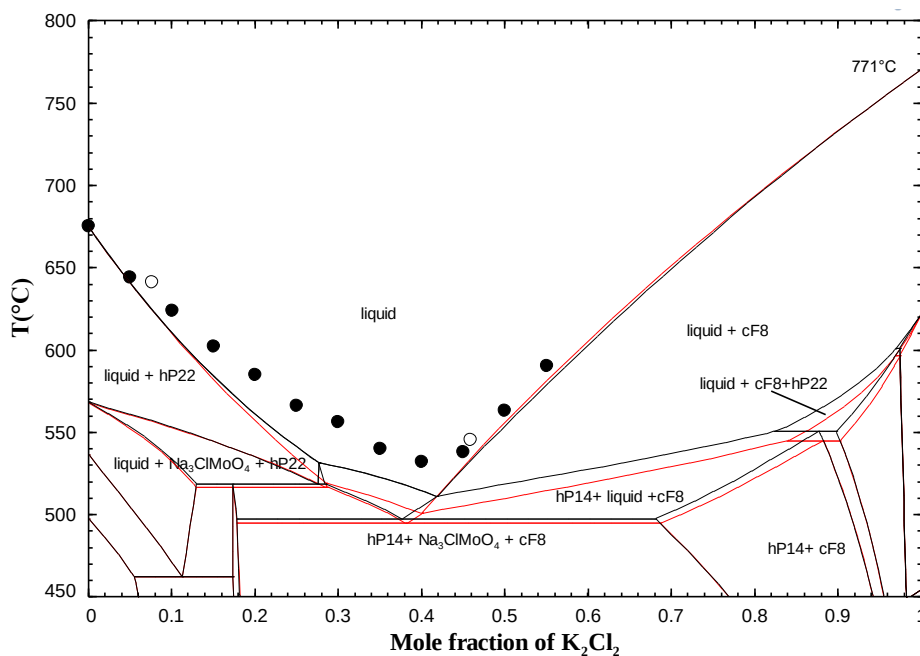


Figure 8.27 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system

$((\text{Na}_2\text{MoO}_4)_{0.85}(\text{K}_2\text{MoO}_4)_{0.15}-\text{K}_2\text{Cl}_2$, section IX). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

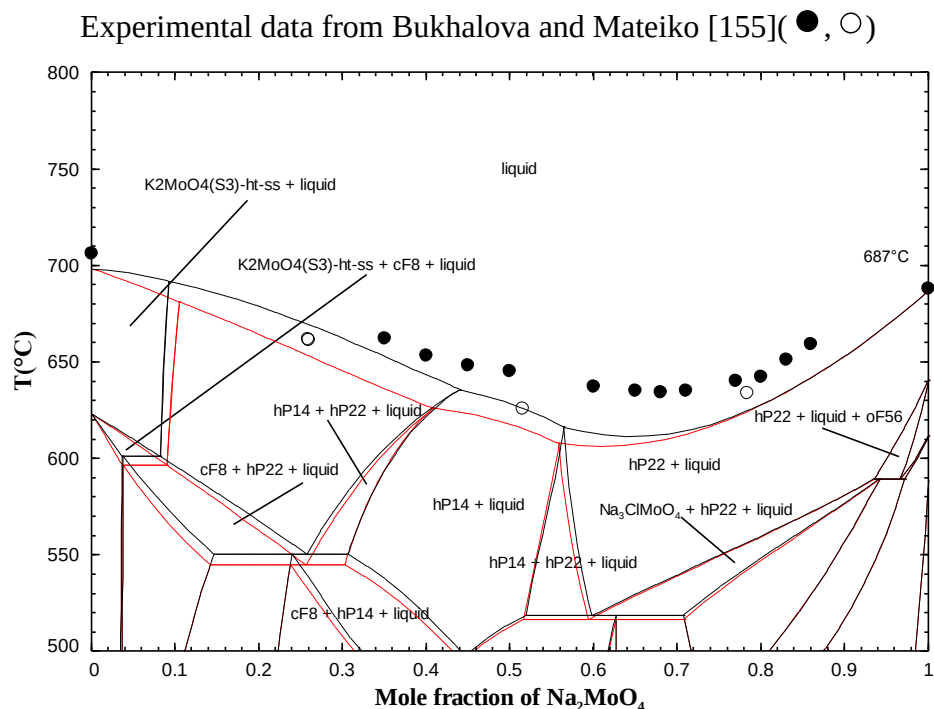


Figure 8.28 Calculated isoplethal section in the $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4)$ system $((\text{K}_2\text{Cl}_2)_{0.35}(\text{K}_2\text{MoO}_4)_{0.65}-\text{Na}_2\text{MoO}_4$, section XIII). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [155] (●, ○)

8.9 Multicomponent system $(\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O})$ (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 Na_2MoO_4 - and K_2MoO_4 -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 $(\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4)$ system, whereas one small ternary reciprocal parameter was required for the $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4)$ system. In our previous work [75],

satisfactory predictions were obtained in the ($\text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4$), ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$), ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$), and ($\text{NaCl} + \text{KCl} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) systems, while one small ternary excess parameter and three small ternary reciprocal parameters were necessary for the ($\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$) and ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) systems, respectively. For all ternary and ternary reciprocal sub-systems evaluated in the present work and previously [39-41, 75], 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, $\text{K}_2\text{MoO}_{4(\text{S3})}$ -ht-ss, $\text{Na}_2\text{MoO}_{4(\text{S2})}$ -ss-rich, $\text{K}_2\text{Cr}_2\text{O}_{7(\text{S.S})}$, aP44 and aP22) were modeled in this study and previously [39-41, 75] 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 $\text{K}_2\text{MoO}_{4(\text{S3})}$ -ht-ss were satisfactorily reproduced in the ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) and ($\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$) systems without introducing any additional parameters in the models for those solid solutions. Similarly, in our previous work [75], measured phase equilibria involving hP22, hP14 and oP28 were satisfactorily reproduced in the ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) and ($\text{NaCl} + \text{KCl} + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$) systems without any additional parameters. Therefore, the developed thermodynamic model is expected to predict accurately phase equilibria in the multicomponent system.

8.10 Conclusions

A thorough critical evaluation of all available phase diagram and thermodynamic data for all condensed phases of the ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) system was conducted in the present study and previously [39, 41, 75], and optimized model parameters were obtained. Since the reactions $2 \text{A}_2\text{MO}_4 = \text{A}_2\text{M}_2\text{O}_7 + \text{A}_2\text{O}$ (where $\text{A} = \text{Na, K}$ and $\text{M} = \text{Cr, Mo}$) are very limited up to above the liquidus temperatures [34], 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 ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{MoO}_4$), ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$), ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$), ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$), ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{MoO}_4$), and ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$).

No solid solubility was introduced at low temperatures in ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{MoO}_4$) since our DSC thermal arrests were consistent with solid-solid transitions for the Na_2CO_3 and Na_2MoO_4 pure compounds. In ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$), overall our DSC results for Na_2MoO_4 -rich compositions agreed with the experimental data from the literature. Owing to the same crystal structure and space group of $\text{Na}_2\text{SO}_{4(\text{S}1)}$ and $\text{Na}_2\text{CrO}_{4(\text{S}1)}$, the ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$) and ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) phase diagrams were modeled simultaneously; two Na_2MoO_4 -rich solid solutions ($\text{Na}_2\text{MoO}_{4(\text{S}2)}$ -ss-rich and cF56) were introduced at intermediate temperatures. In ($\text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4$), 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 [42] 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.

8.11 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.

CHAPITRE 9 DISCUSSION GÉNÉRALE

Le nouveau modèle thermodynamique développé dans le cadre de ce projet doctoral a pour objectif principal de mieux comprendre les phénomènes de formation de dépôts de sels (solides et/ou liquides) intervenant dans les installations à base d'acier et d'acier inoxydable contenant les éléments d'alliage Ni, Cr, Mo, W et V. Il est particulièrement adapté aux environnements riches en sels alcalins, dans lesquels la corrosion chaude pourrait se produire à haute température (entre 600 et 950°C) [14, 57, 58] lors des processus de production d'énergie par combustion.

Parmi les sels alcalins révélés dans ces conditions opérationnelles figurent les chromates et dichromates de sodium et de potassium (Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$ et $\text{K}_2\text{Cr}_2\text{O}_7$), les molybdates et dimolybdates de sodium et de potassium (Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$ et $\text{K}_2\text{Mo}_2\text{O}_7$), et les tungstates et ditungstates de sodium et de potassium (Na_2WO_4 , K_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$ et $\text{K}_2\text{W}_2\text{O}_7$).

Lors du développement du modèle thermodynamique, la première étape a consisté en l'évaluation des propriétés thermodynamiques ($\Delta H_{298.15\text{ K}}^\circ$, $S_{298.15\text{ K}}^\circ$ et C_P) de tous les allotropes et du liquide pur de chacun de ces douze composés. Des recherches approfondies ont aussi été menées sur les structures cristallines et groupes d'espace des différents allotropes, afin de pouvoir identifier plus aisément les solutions solides susceptibles de se former en présence des autres sels pertinents étudiés. En particulier, nos mesures de DRX à haute température ont montré que le composé K_2MoO_4 présente seulement trois allotropes; ce qui contredit les quatre allotropes parfois rapportés dans la littérature.

Les propriétés thermodynamiques des 12 composés purs ont été obtenues à partir d'une évaluation critique de toutes les données expérimentales disponibles dans la littérature. De plus, la DSC-TGA a été utilisée pour mesurer les propriétés de transition solide-solide et de fusion des 6 composés A_2MO_4 (où A = Na ou K, et M = Cr, Mo ou W). Les températures de transition solide-solide et de fusion sélectionnées pour ces composés purs ont été obtenues à l'aide d'une moyenne pondérée, prenant en compte les données de la littérature jugées les plus fiables ainsi que nos mesures de DSC-TGA (relatives aux 2^{ème} et 3^{ème} cycles de chauffe) dans le cas des composés A_2MO_4 . Cette pondération a été basée sur la précision de chaque technique expérimentale. La même méthode a été utilisée pour estimer les variations d'enthalpie.

Comme les données thermodynamiques disponibles pour certains composés $A_2M_2O_7$ (où $A = Na$ ou K , et $M = Cr, Mo$ ou W) étaient parfois limitées, il a été nécessaire de procéder à des estimations à plusieurs reprises. Par exemple, les capacités calorifiques C_P des composés $Na_2Cr_2O_{7(S1)}$, $Na_2Cr_2O_{7(S2)}$ et $K_2Cr_2O_{7(S2)}$ ont été directement dérivées des mesures de $(H_T - H_{298.15K})$ de Nguyen-Duy et Dancy [202], qui étaient très douteuses pour les phases $Na_2Cr_2O_{7(L)}$ et $K_2Cr_2O_{7(L)}$. Des mesures directes de capacité calorifique ou de variation d'enthalpie en fonction de la température devraient être effectuées pour les trois phases solides ci-dessus dans les gammes de température appropriées. La température de fusion sélectionnée pour $K_2Mo_2O_7$ a été basée sur les mesures calorimétriques de Suponitskiy et al [168], qui avaient également mis en évidence une transition de phases solide-solide. Il est possible qu'elle soit significativement trop élevée. En effet, pour le système binaire ($K_2MoO_4 + K_2Mo_2O_7$), bien que le liquidus expérimental de K_2MoO_4 soit bien reproduit par le modèle jusqu'à environ 80% molaire de $K_2Mo_2O_7$, la température eutectique calculée est de 527°C, comparativement à une valeur expérimentale voisine de 480°C.

Les propriétés thermodynamiques sélectionnées pour les composés $A_2M_2O_7$ sont donc moins précises que celles pour les composés A_2MO_4 (où $A = Na$ ou K , et $M = Cr, Mo$ ou W) principalement à cause du manque de données expérimentales. Nous avons pu évaluer les variations d'énergie de Gibbs en fonction de la température pour les réactions du type $2 A_2MO_4 = A_2M_2O_7 + A_2O$. Les températures d'inversion auxquelles ces variations d'énergie de Gibbs s'annulent puis deviennent négatives sont toujours supérieures à 3976°C (valeur estimée pour $Na_2Mo_2O_7$). Cela nous a permis de conclure que ces réactions sont très limitées sur la gamme de température d'intérêt pour les applications industrielles envisagées (i.e. jusqu'aux températures de liquidus). Cela justifie que nous n'ayons considéré que des quantités diluées de Na_2O et K_2O dans notre modèle pour la phase liquide.

La deuxième étape de cette étude a consisté en l'ajout des anions CrO_4^{2-} , $Cr_2O_7^{2-}$, MoO_4^{2-} , et $Mo_2O_7^{2-}$ au modèle thermodynamique développé précédemment par Lindberg et al [39-41] pour le système ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7$). Les paramètres de modèles optimisés par Lindberg et al ont été utilisés directement dans le cadre de cette étude. Nous avons ainsi obtenu un modèle thermodynamique pour le système ($NaCl + Na_2CO_3 + Na_2SO_4$

+ $\text{Na}_2\text{S}_2\text{O}_7$ + Na_2CrO_4 + $\text{Na}_2\text{Cr}_2\text{O}_7$ + Na_2MoO_4 + $\text{Na}_2\text{Mo}_2\text{O}_7$ + Na_2O + KCl + K_2CO_3 + K_2SO_4 + $\text{K}_2\text{S}_2\text{O}_7$ + K_2CrO_4 + $\text{K}_2\text{Cr}_2\text{O}_7$ + K_2MoO_4 + $\text{K}_2\text{Mo}_2\text{O}_7$ + K_2O) (dilué en oxydes libres). L'ajout des ions WO_4^{2-} et $\text{W}_2\text{O}_7^{2-}$ a été initié mais n'a pas pu être finalisé par manque de temps. Nous avons effectué une analyse critique détaillée de toutes les données thermodynamiques disponibles (principalement diagrammes de phases) issues de la littérature pour tous les sous-systèmes pertinents : sous-systèmes binaires à ion commun, sous-systèmes ternaires à cation commun (Na^+ ou K^+), sous-systèmes ternaires réciproques (avec les deux cations Na^+ et K^+ , et deux anions), et sous-systèmes d'ordre supérieur. Le MQMQA a été utilisé pour la phase liquide, ainsi que pour la solution solide hexagonale de haute température hP22 (Na_2CO_3 + Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4 + K_2CO_3 + K_2SO_4 + K_2CrO_4 + $[\text{K}_2\text{MoO}_4]$) avec une solubilité partielle de K_2MoO_4 et une solubilité mutuelle complète pour les autres sels. Les autres solutions solides ont toutes été modélisées à l'aide du CEF.

Nous avons ainsi modélisé 23 sous-systèmes binaires à ion commun (11 à base de CrO_4 ou Cr_2O_7 , et 12 à base de MoO_4 ou Mo_2O_7).

De façon à pouvoir mieux calibrer notre modèle, nous avons effectué des expériences de DSC-TGA pour plusieurs sous-systèmes binaires à ion commun dans des gammes de composition pertinentes. Ainsi, 19 expériences de DSC-TGA ont été réalisées pour trois sous-systèmes binaires à base de chromates : 5 compositions dans le système (Na_2CO_3 + Na_2CrO_4), 4 compositions dans le système (K_2CO_3 + K_2CrO_4), et 10 compositions dans le système (Na_2CrO_4 + K_2CrO_4).

D'autre part, 37 expériences de DSC-TGA ont été effectuées pour six sous-systèmes binaires à base de molybdates : 8 compositions dans le système (Na_2CO_3 + Na_2MoO_4) (en présence ou non de $\text{CO}_2(\text{g})$), 5 compositions dans le système (Na_2SO_4 + Na_2MoO_4), 5 compositions dans le système (K_2SO_4 + K_2MoO_4) (dont une dupliquée), 5 compositions dans le système (Na_2CrO_4 + Na_2MoO_4), 3 compositions dans le système (K_2CrO_4 + K_2MoO_4), et 11 compositions dans le système (Na_2MoO_4 + K_2MoO_4).

Nos mesures de DSC-TGA pour le système (Na_2CO_3 + Na_2MoO_4) ont montré qu'en absence de $\text{CO}_2(\text{g})$, les températures de liquidus étaient sous-estimées; ce qui a été attribué à une dissociation partielle de $\text{Na}_2\text{CO}_3(\text{s})$ pour former $\text{Na}_2\text{O}(\text{l})$ (dissous dans la solution liquide) et $\text{CO}_2(\text{g})$. Nos calculs

ont montré que cette dissociation est très limitée (fraction molaire de $\text{Na}_2\text{O}_{(\text{L})}$ inférieure à 10^{-8} pour $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{MoO}_4)$ et $(\text{Na}_2\text{CO}_3 + \text{Na}_2\text{CrO}_4)$). De manière similaire, dans les systèmes $(\text{K}_2\text{CO}_3 + \text{K}_2\text{MoO}_4)$ et $(\text{K}_2\text{CO}_3 + \text{K}_2\text{CrO}_4)$, $\text{K}_2\text{CO}_{3(\text{S}2)}$ peut se décomposer partiellement pour former $\text{K}_2\text{O}_{(\text{L})}$ (dissous dans la solution liquide) et $\text{CO}_{2(\text{g})}$, mais la fraction molaire calculée de $\text{K}_2\text{O}_{(\text{L})}$ demeure voisine de 10^{-10} seulement.

Les phases non-stœchiométriques de glasérite de chrome $\text{K}_3\text{Na}(\text{CrO}_4)_2$ et de glasérite de molybdène $\text{K}_3\text{Na}(\text{MoO}_4)_2$ ont été étudiées afin de mieux caractériser la gamme de compositions de la solution solide hP14 et d'identifier ses limites de phases. Deux échantillons avec les compositions initiales (45% molaire Na_2CrO_4 + 55% molaire K_2CrO_4) et (35% molaire Na_2MoO_4 + 65% molaire K_2MoO_4) ont été analysés par SEM-EDS et DSC-TGA après avoir subi un recuit à 400°C pendant trois semaines pour la glasérite de chrome et pendant quatre semaines pour la glasérite de molybdène.

Pour confirmer la formation des phases $\text{K}_3\text{Na}(\text{CrO}_4)_2$ et $\text{K}_3\text{Na}(\text{MoO}_4)_2$, un total de 20 et 6 analyses EDS ont été réalisées respectivement. Les résultats obtenus ont permis de confirmer que les phases équilibrées étaient toutes deux globalement homogènes. En effet, la composition estimée de la phase équilibrée de glasérite de chrome était $\text{Na}_{1.03}\text{K}_{1.13}\text{Cr}_{1.05}\text{O}_{3.92}$, comparée à la composition initiale du mélange mécanique de $\text{Na}_{0.9}\text{K}_{1.1}\text{Cr}_1\text{O}_4$. De même, la composition estimée de la phase équilibrée de glasérite de molybdène était $\text{K}_{1.29}\text{Na}_{0.70}\text{Mo}_{0.98}\text{O}_{3.92}$, alors que la composition du mélange mécanique original était de $\text{K}_{1.3}\text{Na}_{0.7}\text{Mo}_1\text{O}_4$.

Les données de diagrammes de phases étaient très limitées pour les sous-systèmes binaires à base de dichromate ou dimolybdate de sodium et potassium. A notre connaissance, des données expérimentales n'étaient disponibles que pour les systèmes $(\text{KCl} + \text{K}_2\text{Cr}_2\text{O}_7)$, $(\text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7)$, $(\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7)$, $(\text{Na}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Cr}_2\text{O}_7)$, $(\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{Mo}_2\text{O}_7)$, $(\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7)$ et $(\text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7)$.

Le liquide binaire $(\text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7)$ a été supposé idéal de façon à reproduire le diagramme de phases expérimental de Groschuff [131]. Cette hypothèse a également permis de très bien

reproduire les mesures de Flood et Muan [254], relatives à la teneur en $\text{K}_2\text{Cr}_2\text{O}_7$ du liquide ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{CrO}_4$) en fonction de la température (entre 610 et 760°C), à saturation en Cr_2O_3 et à une pression partielle de $\text{O}_{2(\text{g})}$ de 1 atm ou 0.21 atm.

Jusqu'à présent, le diagramme de phases du sous-système binaire ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7$) n'a pas été mesuré. Nous avons conclu qu'il faudrait faire des choix arbitraires pour reproduire les mesures de Flood et Muan [254], correspondant à la teneur en $\text{Na}_2\text{Cr}_2\text{O}_7$ du liquide binaire en fonction de la température (entre 400 et 550°C), à saturation en Cr_2O_3 et à une pression partielle de $\text{O}_{2(\text{g})}$ de 1 atm. Ainsi, il faudrait potentiellement ajuster les propriétés thermodynamiques de $\text{Cr}_2\text{O}_{3(\text{s})}$ et/ou $\text{Na}_2\text{Cr}_2\text{O}_{7(\text{L})}$ (i.e. déstabilisation d'au moins l'un de ces composés), et introduire une déviation positive (par rapport à l'idéalité) pour le liquide ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7$). Finalement, ce liquide a lui-aussi été supposé idéal par analogie avec le liquide ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$). Il est recommandé de mesurer le diagramme de phases ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7$) de façon à pouvoir mieux calibrer le liquide correspondant.

Le liquide binaire ($\text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7$) a été supposé idéal; ce qui a permis de reproduire de manière satisfaisante le liquidus expérimental de K_2MoO_4 jusqu'à environ 80% molaire de $\text{K}_2\text{Mo}_2\text{O}_7$. Néanmoins, comme nous l'avons déjà discuté auparavant, la température eutectique est surestimée par notre modèle; ce qui pourrait être dû au choix d'une température de fusion trop élevée pour $\text{K}_2\text{Mo}_2\text{O}_7$.

Une déviation positive par rapport à l'idéalité a été introduite pour le liquide ($\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7$) de façon à reproduire au mieux les données expérimentales de diagramme de phases (en particulier, celles de Groschuff [271]).

Les données de diagrammes de phases étaient assez limitées pour les sous-systèmes ternaires à cation commun (Na^+ ou K^+), les sous-systèmes ternaires réciproques (impliquant Na^+ , K^+ et deux anions) et les sous-systèmes d'ordre supérieur à base de Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 et/ou K_2MoO_4 . Des données étaient disponibles pour les systèmes ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4$), ($\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{CrO}_4$), ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4$), ($\text{NaCl} + \text{KCl} + \text{Na}_2\text{CrO}_4 +$

K_2CrO_4), ($Na_2CO_3 + K_2CO_3 + Na_2CrO_4 + K_2CrO_4$), ($Na_2CO_3 + K_2CO_3 + Na_2SO_4 + K_2SO_4 + Na_2CrO_4 + K_2CrO_4$), ($Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4$), et ($NaCl + KCl + Na_2MoO_4 + K_2MoO_4$). Pour la plupart de ces systèmes, des prédictions satisfaisantes ont été obtenues à partir des paramètres de modèles optimisés pour les sous-systèmes binaires à ion commun. Pour trois d'entre eux, de petits paramètres en excès ternaires ou ternaires réciproques ont dû être introduits : 1 paramètre pour ($K_2CO_3 + K_2SO_4 + K_2CrO_4$) ainsi que pour ($NaCl + KCl + Na_2MoO_4 + K_2MoO_4$), et 3 paramètres pour ($Na_2CO_3 + K_2CO_3 + Na_2CrO_4 + K_2CrO_4$). Pour le système quaternaire réciproque ($Na_2CO_3 + K_2CO_3 + Na_2SO_4 + K_2SO_4 + Na_2CrO_4 + K_2CrO_4$), des déviations importantes ont parfois été observées entre les calculs et les mesures expérimentales. Néanmoins, ces dernières ont été jugées peu fiables, à cause de l'extraction graphique requise et aussi à cause de l'écart observé pour certains mélanges binaires ($Na_2CO_3 + Na_2SO_4$).

Pour le sous-système ternaire à cation commun ($KCl + K_2CO_3 + K_2CrO_4$), un eutectique ternaire a été prédit à la composition (54.7% molaire KCl + 27.8% molaire K_2CO_3 + 17.5% molaire K_2CrO_4) et à 593°C. Nous avons mesuré par DSC-TGA un arrêt thermique unique vers 596°C à la composition (55.0% molaire KCl + 28.0% molaire K_2CO_3 + 17.0% molaire K_2CrO_4). La prédiction de cet eutectique ternaire est donc excellente, permettant ainsi d'évaluer le risque de corrosion « catastrophique » associé à la formation d'une phase liquide à basse température.

Pour tous les sous-systèmes ternaires à cation commun (Na^+ ou K^+) et ternaires réciproques évalués dans ce travail et dans les travaux antérieurs [39-41], aucun ou seulement de petits paramètres ternaires ou ternaires réciproques ont été requis pour reproduire de manière satisfaisante les données expérimentales disponibles. Il est donc raisonnable de supposer que les prédictions de notre modèle thermodynamique sont satisfaisantes pour tous les sous-systèmes ternaires et ternaires réciproques pour lesquels aucune mesure n'est disponible. Nous nous attendons donc à ce que notre modèle permette d'obtenir des prédictions fiables pour la phase liquide ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + Na_2CrO_4 + Na_2Cr_2O_7 + Na_2MoO_4 + Na_2Mo_2O_7 + Na_2O + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7 + K_2CrO_4 + K_2Cr_2O_7 + K_2MoO_4 + K_2Mo_2O_7 + K_2O$) (diluée en oxydes libres).

Plusieurs solutions solides multicomposantes (hP22, oS28, oP28, hP14, oF56, cF56, $K_2MoO_{4(S3)}$ -ht-ss, $Na_2MoO_{4(S2)}$ -ss-rich, $K_2Cr_2O_7(s.s)$, aP44 et aP22) ont été modélisées dans cette étude et dans des travaux antérieurs [39-41].

Dans ce travail, les équilibres de phases expérimentaux impliquant hP22, hP14 et oP28 ont pu être reproduits de manière satisfaisante dans les sous-systèmes ternaires réciproques ($Na_2SO_4 + K_2SO_4 + Na_2CrO_4 + K_2CrO_4$) et ($NaCl + KCl + Na_2CrO_4 + K_2CrO_4$), sans avoir besoin de paramètres de modèles supplémentaires (pour les solutions solides). Il en est de même pour les équilibres de phases expérimentaux impliquant hP22, hP14 et $K_2MoO_{4(S3)}$ -ht-ss dans les sous-systèmes ($Na_2SO_4 + Na_2CrO_4 + Na_2MoO_4$) et ($NaCl + KCl + Na_2MoO_4 + K_2MoO_4$). Nous nous attendons donc à ce que le modèle thermodynamique développé puisse prédire de manière fiable les équilibres de phases dans le système multicomposant à 18 constituants (dilué en Na_2O et en K_2O).

CHAPITRE 10

CONCLUSION ET RECOMMANDATIONS

Dans le cadre de ce projet de recherche, nous avons développé un modèle thermodynamique pour le système ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{MoO}_4 + \text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{O} + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 + \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{MoO}_4 + \text{K}_2\text{Mo}_2\text{O}_7 + \text{K}_2\text{O}$) (dilué en Na_2O et en K_2O). Nous avons ajouté les chromates, dichromates, molybdates et dimolybdates de sodium et de potassium au modèle thermodynamique précédemment développé par Lindberg et al pour le système ($\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_7 + \text{KCl} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7$) [39-41]. L'ajout des tungstates et ditungstates de sodium et de potassium est bien avancée mais n'a pas pu être finalisée par manque de temps.

Notre revue de la littérature approfondie a permis d'avoir une meilleure vision des mécanismes réactionnels dans des environnements riches en sels alcalins ((NaCl , KCl , Na_2SO_4 , K_2SO_4 , Na_2CO_3 , K_2CO_3 , $\text{Na}_2\text{S}_2\text{O}_7$, et $\text{K}_2\text{S}_2\text{O}_7$ [28]), (Na_2CrO_4 et K_2CrO_4 [29-31]), (Na_2MoO_4 [30-32] et K_2MoO_4 [31]), (Na_2WO_4 [30, 31, 33] et K_2WO_4 [31]), et ($\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{W}_2\text{O}_7$, et $\text{K}_2\text{W}_2\text{O}_7$ [34])).

Notre modèle permet de mieux comprendre les réactions chimiques de corrosion chaude à haute température (entre 600 et 950°C) [14, 57, 58] dans les procédés de production d'énergie par combustion. En particulier, il permet de mieux évaluer les risques de corrosion « catastrophique » (i.e. formation d'une phase liquide) en analysant la formation des différentes phases dans des environnements riches en sels alcalins ainsi que les interactions entre ces phases. Il est ainsi possible d'effectuer des calculs fiables susceptibles d'améliorer un grand nombre de procédés industriels connexes, en optimisant leurs paramètres opérationnels de façon à augmenter leur efficacité énergétique et environnementale.

Dans un premier temps, nous avons estimé les propriétés thermodynamiques (enthalpie standard $\Delta H_{298.15\text{ K}}^\circ$ à 298.15 K, entropie standard $S_{298.15\text{ K}}^\circ$ à 298.15 K, et capacité calorifique C_p en fonction de la température) des phases solides et liquides des composés purs A_2MO_4 et $\text{A}_2\text{M}_2\text{O}_7$ (où $\text{A} = \text{Na}$ ou K , et $\text{M} = \text{Cr}$, Mo ou W). Pour ce faire, nous avons évalué de manière critique toutes les données expérimentales disponibles dans la littérature scientifique pertinente. Nous avons également pris en compte nos expériences de DSC-TGA, qui nous ont permis de mesurer les températures et variations d'enthalpie des transitions de phases solide-solide et de fusion pour les six composés A_2MO_4 (où $\text{A} = \text{Na}$ ou K , et $\text{M} = \text{Cr}$, Mo ou W).

Les structures cristallines et groupes d'espace de tous les allotropes des douze composés purs A_2MO_4 et $A_2M_2O_7$ (où $A = Na$ ou K , et $M = Cr$, Mo ou W) ont été identifiés grâce à une revue de la littérature approfondie; ce qui nous a permis d'identifier plus aisément les solutions solides pouvant se former avec les autres sels considérés dans ce travail.

Dans un deuxième temps, nous avons ajouté les chromates et dichromates de sodium et de potassium, puis les molybdates et dimolybdates de sodium et de potassium au modèle thermodynamique existant pour le système ($NaCl + Na_2CO_3 + Na_2SO_4 + Na_2S_2O_7 + KCl + K_2CO_3 + K_2SO_4 + K_2S_2O_7$) [39-41]. Le modèle thermodynamique a été développé à l'aide de l'approche CALPHAD (CALculation of PHase Diagrams). Tous les sous-systèmes binaires à ion commun pertinents ont été modélisés, et des prédictions ont ensuite été faites pour les sous-systèmes d'ordre supérieur à l'aide de techniques d'interpolation appropriées. Des paramètres ternaires ou ternaires réciproques (de faible amplitude) ont parfois été introduits de façon à reproduire au mieux les mesures expérimentales disponibles. La phase liquide et la solution solide hexagonale de haute température (hP22) ont été modélisées avec le MQMQA. Toutes les autres solutions solides ont été modélisées avec le CEF. Pour mieux calibrer le modèle, des expériences de DSC-TGA ont été effectuées à différentes compositions dans les sous-systèmes binaires à ion commun ($Na_2CO_3 + Na_2CrO_4$), ($K_2CO_3 + K_2CrO_4$), ($Na_2CrO_4 + K_2CrO_4$), ($Na_2CO_3 + Na_2MoO_4$), ($Na_2SO_4 + Na_2MoO_4$), ($K_2SO_4 + K_2MoO_4$), ($Na_2CrO_4 + Na_2MoO_4$), ($K_2CrO_4 + K_2MoO_4$), et ($Na_2MoO_4 + K_2MoO_4$). En particulier, nous avons étudié la gamme de composition de la solution solide de glasérite de chrome $K_3Na(CrO_4)_2$. Des expériences de DSC-TGA ont été conduites pour des mélanges mécaniques des réactifs prétraités ainsi que pour un échantillon équilibré (dont l'homogénéité globale avait été confirmée par des analyses EDS-SEM), auquel un excès de Na_2CrO_4 ou K_2CrO_4 avait été ajouté subséquemment. La solution solide de glasérite de molybdène $K_3Na(MoO_4)_2$ a été étudiée avec une approche similaire. Finalement, la DSC-TGA nous a permis de confirmer l'existence d'un eutectique ternaire dans le sous-système ternaire à cation commun ($KCl + K_2CO_3 + K_2CrO_4$).

Le modèle thermodynamique développé reproduit en deçà des marges d'erreur expérimentales les données issues de la littérature (principalement diagrammes de phases) ainsi que nos mesures expérimentales de DSC-TGA. Il est compatible avec le logiciel thermochimique FactSage [42], qui

inclut un algorithme de minimisation de l'énergie de Gibbs. Les propriétés thermodynamiques de la phase liquide multicomposante peuvent être prédites de manière fiable à partir des paramètres optimisés pour les sous-systèmes binaires à ion commun, ternaires à cation commun (Na^+ ou K^+), et ternaires réciproques.

Comme nous l'avons déjà indiqué précédemment, l'ajout des tungstates et ditungstates de sodium et de potassium n'a malheureusement pas pu être finalisé par manque de temps. Il est recommandé de terminer ce travail déjà bien avancé. En effet, des optimisations préliminaires ont déjà été réalisées pour les sous-systèmes binaires à ion commun ($\text{NaCl} + \text{Na}_2\text{WO}_4$), ($\text{KCl} + \text{K}_2\text{WO}_4$), ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{WO}_4$), ($\text{K}_2\text{CO}_3 + \text{K}_2\text{WO}_4$), ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{WO}_4$), ($\text{K}_2\text{SO}_4 + \text{K}_2\text{WO}_4$), ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{WO}_4$), ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{WO}_4$), et ($\text{Na}_2\text{WO}_4 + \text{K}_2\text{WO}_4$). Nous avons effectué 35 mesures de DSC-TGA dans les sous-systèmes binaires ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{WO}_4$), ($\text{K}_2\text{SO}_4 + \text{K}_2\text{WO}_4$), ($\text{Na}_2\text{CrO}_4 + \text{Na}_2\text{WO}_4$), ($\text{K}_2\text{CrO}_4 + \text{K}_2\text{WO}_4$), ($\text{Na}_2\text{MoO}_4 + \text{Na}_2\text{WO}_4$), et ($\text{Na}_2\text{WO}_4 + \text{K}_2\text{WO}_4$). Pour nos optimisations préliminaires, nous avons pris en compte à la fois les données expérimentales issues de la littérature jugées les plus fiables et nos propres mesures de DSC-TGA.

Nos résultats actuels montrent que les sous-systèmes binaires à base de tungstates ($\text{NaCl} + \text{Na}_2\text{WO}_4$), ($\text{KCl} + \text{K}_2\text{WO}_4$), ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{WO}_4$) et ($\text{K}_2\text{CO}_3 + \text{K}_2\text{WO}_4$) présentent des comportements très similaires à ceux des sous-systèmes binaires correspondants à base de molybdates, à savoir ($\text{NaCl} + \text{Na}_2\text{MoO}_4$), ($\text{KCl} + \text{K}_2\text{MoO}_4$), ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{MoO}_4$) et ($\text{K}_2\text{CO}_3 + \text{K}_2\text{MoO}_4$), respectivement.

La présence de la phase de glasérite de tungstène $\text{K}_3\text{Na}(\text{WO}_4)_2$ a été identifiée dans le sous-système binaire ($\text{Na}_2\text{WO}_4 + \text{K}_2\text{WO}_4$). Nous avons procédé à un recuit à 400°C pendant quatre semaines avant de mesurer expérimentalement les équilibres de phases solide-solide à basse température par DSC-TGA. Nous avons adopté la même méthodologie que celle utilisée pour les glasérites de chrome et de molybdène pour caractériser le domaine de composition de cette phase. La technique EDS-SEM a permis de confirmer l'homogénéité globale de la solution solide non-stœchiométrique de glasérite de tungstène équilibrée avec une composition originale de (35% molaire Na_2WO_4 + 65% molaire K_2WO_4). Par ailleurs, nous avons pu identifier dans le sous-système binaire ($\text{Na}_2\text{WO}_4 + \text{K}_2\text{WO}_4$) deux composés à fusion incongruente ($2\text{Na}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$ et $\text{Na}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$).

L'existence de ces deux composés avait été préalablement rapportée par Bukhalova and Mateiko [169].

Les compositions $2\text{Na}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$ et $\text{Na}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$ avaient été recuites à 545°C pendant 2 semaines afin d'assurer leur homogénéisation. Ensuite, les deux échantillons équilibrés avaient été refroidis à l'air, broyés mécaniquement et finalement analysés par SEM-EDS et DSC-TGA.

Notre revue de la littérature a révélé un manque de données de diagrammes de phases pour les sous-systèmes binaires à base de ditungstates. A notre connaissance, des données expérimentales sont seulement disponibles pour les sous-systèmes binaires à ion commun ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{W}_2\text{O}_7$), ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{W}_2\text{O}_7$) et ($\text{Na}_2\text{Mo}_2\text{O}_7 + \text{Na}_2\text{W}_2\text{O}_7$).

D'autres améliorations du modèle thermodynamique actuel sont envisageables. Les dichromates ($\text{Na}_2\text{Cr}_2\text{O}_7$ et $\text{K}_2\text{Cr}_2\text{O}_7$), dimolybdates ($\text{Na}_2\text{Mo}_2\text{O}_7$ et $\text{K}_2\text{Mo}_2\text{O}_7$) et ditungstates ($\text{Na}_2\text{W}_2\text{O}_7$ et $\text{K}_2\text{W}_2\text{O}_7$) n'ont pas été suffisamment étudiés dans la littérature en termes de propriétés thermodynamiques et de structures cristallines. Pour pallier ce manque de données, des analyses DRX pourraient être effectuées à température ambiante et à haute température, afin de caractériser les allotropes de chaque composé pur pertinent. Il serait également possible de réaliser des expériences pour mesurer expérimentalement l'enthalpie standard $\Delta H_{298.15\text{ K}}^\circ$ à 298.15 K (par calorimétrie), l'entropie standard $S_{298.15\text{ K}}^\circ$ à 298.15 K (pouvant être dérivée de mesures de C_P à basse température), et la capacité calorifique C_P . De plus, des mesures de DSC-TGA permettraient d'estimer les températures et variations d'enthalpie pour les transitions de phases solide-solide et la fusion.

En ce qui concerne les vanadates, les données de diagrammes de phases sont pratiquement inexistantes actuellement. Nous avons constaté que des valeurs sont disponibles pour les propriétés thermodynamiques de NaVO_3 , Na_3VO_4 et $\text{Na}_2\text{V}_2\text{O}_7$ dans la compilation de Barin [127]. Il serait pertinent de réaliser une étude cristallographique par DRX pour ces composés, ainsi que mesurer expérimentalement leurs propriétés thermodynamiques, comme nous l'avons déjà recommandé pour les composés purs $\text{A}_2\text{M}_2\text{O}_7$ (où $\text{A} = \text{Na}$ ou K , et $\text{M} = \text{Cr}$, Mo ou W).

RÉFÉRENCES

- [1] J.-J. Remeau and H. Barthelemy, "Quelques problèmes de corrosion dans la fabrication de la pâte à papier par le procédé kraft," *Matériaux & Techniques*, vol. 66, no. 11-12, pp. 383-385, 1978.
- [2] E. Vakkilainen, *Kraft recovery boilers – Principles and practice*. 2005.
- [3] Y. Kawahara, "Application of High Temperature Corrosion-Resistant Materials and Coatings Under Severe Corrosive Environment in Waste-to-Energy Boilers," *Journal of Thermal Spray Technology*, vol. 16, no. 2, pp. 202-213, 2007, doi: 10.1007/s11666-006-9012-5.
- [4] Y. Kawahara, "Development and application of high-temperature corrosion-resistant materials and coatings for advanced waste-to-energy plants," *Materials at High Temperatures*, vol. 14, no. 3, pp. 261-268, 1997.
- [5] B. A. Pint, "High-Temperature Corrosion in Fossil Fuel Power Generation: Present and Future," *JOM*, vol. 65, no. 8, pp. 1024-1032, 2013, doi: 10.1007/s11837-013-0642-z.
- [6] M. Montgomery, T. Vilhelmsen, and S. A. Jensen, "Potential high temperature corrosion problems due to co-firing of biomass and fossil fuels," *Materials and Corrosion*, <https://doi.org/10.1002/maco.200804166> vol. 59, no. 10, pp. 783-793, 2008, doi: <https://doi.org/10.1002/maco.200804166>.
- [7] G. Sorell, "The role of chlorine in high temperature corrosion in waste-to-energy plants," *Materials at High Temperatures*, vol. 14, no. 3, pp. 207-220, 1997, doi: 10.1080/09603409.1997.11689546.
- [8] R. W. Bryers, "Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels," *Progress in Energy and Combustion Science*, vol. 22, no. 1, pp. 29-120, 1996, doi: [https://doi.org/10.1016/0360-1285\(95\)00012-7](https://doi.org/10.1016/0360-1285(95)00012-7).
- [9] W. Bakker, "High temperature corrosion in coal gasifiers," *Mater. Res. (Sao Carlos, Braz.)*, vol. 7, no. 1, pp. 53-59, 2004, doi: 10.1590/s1516-14392004000100009.
- [10] S. Karlsson, L.-E. Åmand, and J. Liske, "Reducing high-temperature corrosion on high-alloyed stainless steel superheaters by co-combustion of municipal sewage sludge in a fluidised bed boiler," *Fuel*, vol. 139, pp. 482-493, 2015, doi: <https://doi.org/10.1016/j.fuel.2014.09.007>.
- [11] Y. Liu, W. Fan, X. Wu, and X. Zhang, "Chlorine-Induced High-Temperature Corrosion of Boiler Steels Combusting Sha Erhu Coal Compared to Biomass," *Energy & Fuels*, vol. 32, no. 4, pp. 4237-4247, 2018, doi: 10.1021/acs.energyfuels.7b03143.
- [12] M. Oksa, P. Auerkari, J. Salonen, and T. Varis, "Nickel-based HVOF coatings promoting high temperature corrosion resistance of biomass-fired power plant boilers," *Fuel Processing Technology*, vol. 125, pp. 236-245, 2014, doi: <https://doi.org/10.1016/j.fuproc.2014.04.006>.

- [13] D. Bankiewicz, P. Yrjas, and M. Hupa, "High-Temperature Corrosion of Superheater Tube Materials Exposed to Zinc Salts," *Energy & Fuels*, vol. 23, no. 7, pp. 3469-3474, 2009, doi: 10.1021/ef801012z.
- [14] N. Eliaz, G. Shemesh, and R. Latanision, "Hot corrosion in gas turbine components," *Engineering Failure Analysis*, vol. 9, no. 1, pp. 31-43, 2002.
- [15] K. Schofield, "New Method To Minimize High-Temperature Corrosion Resulting from Alkali Sulfate and Chloride Deposition in Combustion Systems. II. Molybdenum Salts," *Energy & Fuels*, vol. 19, no. 5, pp. 1898-1905, 2005, doi: 10.1021/ef050069y.
- [16] J. Stringer, "Hot Corrosion of High-Temperature Alloys," *Annual Review of Materials Science*, vol. 7, no. 1, pp. 477-509, 1977, doi: 10.1146/annurev.ms.07.080177.002401.
- [17] D. A. Shifler, "The Increasing Complexity of Hot Corrosion," *Journal of Engineering for Gas Turbines and Power*, 2017, doi: 10.1115/1.4038037.
- [18] R. Singh and M. B. Venkataraman, "High Temperature Corrosion and Oxidation of Metals," *Metals*, vol. 9, no. 9, p. 942, 2019. [Online]. Available: <https://www.mdpi.com/2075-4701/9/9/942>.
- [19] B. J. Skrifvars, R. Backman, M. Hupa, K. Salmenoja, and E. Vakkilainen, "Corrosion of superheater steel materials under alkali salt deposits Part 1: The effect of salt deposit composition and temperature," *Corrosion Science*, vol. 50, no. 5, pp. 1274-1282, 2008, doi: 10.1016/j.corsci.2008.01.010.
- [20] H. P. Nielsen, F. J. Frandsen, K. Dam-Johansen, and L. L. Baxter, "The implications of chlorine-associated corrosion on the operation of biomass-fired boilers," *Progress in Energy and Combustion Science*, vol. 26, no. 3, pp. 283-298, 2000, doi: [https://doi.org/10.1016/S0360-1285\(00\)00003-4](https://doi.org/10.1016/S0360-1285(00)00003-4).
- [21] J. Goebel, F. Pettit, and G. Goward, "Mechanisms for the hot corrosion of nickel-base alloys," *Metallurgical Transactions*, vol. 4, no. 1, pp. 261-278, 1973.
- [22] A. K. Misra and C. A. Stearns, "Mechanism of corrosion of nickel-base superalloys by molten sodium molybdate(VI) at elevated temperatures," *Natl. Aeronaut. Space Adm.*, 0499-9320, 1983.
- [23] A. K. Misra, "Mechanism of Na₂SO₄-Induced Corrosion of Molybdenum Containing Nickel-Base Superalloys at High Temperatures I. Corrosion in Atmospheres Containing Only," *Journal of the Electrochemical Society*, vol. 133, no. 5, pp. 1029-1038, 1986.
- [24] G. Béranger, J. C. Colson, and F. Dabosi, *Corrosion des matériaux à haute température*. Les Ulis, France: Editions de physique (in Français), 1987.
- [25] A.-M. Huntz and B. Pieraggi, *Oxydation des matériaux métalliques: comportement à haute température*. Hermes-Lavoisier, 2003.
- [26] L. L. Baxter *et al.*, "The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences," *Fuel Processing Technology*, vol. 54, no. 1, pp. 47-78, 1998, doi: [https://doi.org/10.1016/S0378-3820\(97\)00060-X](https://doi.org/10.1016/S0378-3820(97)00060-X).
- [27] M. Paneru, G. Stein-Brzozowska, J. r. Maier, and G. n. Scheffknecht, "Corrosion mechanism of alloy 310 austenitic steel beneath NaCl deposit under varying SO₂

- concentrations in an oxy-fuel combustion atmosphere," *Energy Fuels*, vol. 27, no. 10, pp. 5699-5705, 2013.
- [28] D. Lindberg, "Thermochemistry and melting properties of alkali salt mixtures in black liquor conversion processes," Åbo Akademi University, 2007.
- [29] J. Lehmusto, D. Lindberg, P. Yrjas, B.-J. Skrifvars, and M. Hupa, "Studies on the partial reactions between potassium chloride and metallic chromium concerning corrosion at elevated temperatures," *Oxidation of metals*, vol. 77, no. 3-4, pp. 129-148, 2012.
- [30] G. Fryburg, F. Kohl, and C. Stearns, "Chemical Reactions Involved in the Initiation of Hot Corrosion of IN-738," *Journal Of The Electrochemical Society*, vol. 131, no. 12, pp. 2985-2997, 1984.
- [31] S. Benalia *et al.*, "Critical Evaluation and Calorimetric Study of the Thermodynamic Properties of Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 , and K_2WO_4 ," *Submitted to publication in Journal of Physical and Chemical Reference Data*, 2023.
- [32] G. C. Fryburg, F. J. Kohl, C. A. Stearns, and W. L. Fielder, "Chemical Reactions Involved in the Initiation of Hot Corrosion of B-1900 and NASA-TRW VIA," *Journal of The Electrochemical Society*, vol. 129, no. 3, pp. 571-585, 1982, doi: 10.1149/1.2123928.
- [33] Z. Foroulis and W. Smeltzer, *Metal-slag-gas Reactions and Processes*. Princeton, NJ: Electrothermics and Metallurgy and Corrosion Divisions ..., 1975.
- [34] S. Benalia, P. Chartrand, and C. Robelin, "Critical Evaluation of the Thermodynamic Properties of $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{W}_2\text{O}_7$, and $\text{K}_2\text{W}_2\text{O}_7$," *Submitted to publication in Journal of Physical and Chemical Reference Data*, 2023.
- [35] H. J. Grabke, E. Reese, and M. Spiegel, "The effects of chlorides, hydrogen chloride, and sulfur dioxide in the oxidation of steels below deposits," *Corrosion Science*, vol. 37, no. 7, pp. 1023-1043, 1995, doi: [https://doi.org/10.1016/0010-938X\(95\)00011-8](https://doi.org/10.1016/0010-938X(95)00011-8).
- [36] L. Antoni and A. Galerie, "Corrosion seche des metaux. Cas industriels: depots, milieux fondus," in "Techniques de l'ingénieur. Matériaux métalliques," 2003.
- [37] W. W. Liang, P. L. Lin, and A. D. Pelton, "Analysis and calculation of binary and ternary phase diagrams containing sodium sulfate, sodium chromate(VI), sodium molybdate(VI), and sodium tungstate(VI)," *High Temperature Science*, vol. 12, no. 1, pp. 41-57, 1980.
- [38] W. Liang, P. Lin, and A. Pelton, "ANALYSIS AND CALCULATION OF BINARY AND TERNARY PHASE-DIAGRAMS CONTAINING NaCl , Na_2SO_4 , Na_2CrO_4 , Na_2MoO_4 , AND Na_2WO_4 ," *High Temperature Science*, vol. 12, no. 2, pp. 71-88, 1980.
- [39] D. Lindberg, R. Backman, and P. Chartrand, "Thermodynamic evaluation and optimization of the (Na_2SO_4 + K_2SO_4 + $\text{Na}_2\text{S}_2\text{O}_7$ + $\text{K}_2\text{S}_2\text{O}_7$) system," *Journal of Chemical Thermodynamics*, vol. 38, no. 12, pp. 1568-1583, 2006.
- [40] D. Lindberg, R. Backman, and P. Chartrand, "Thermodynamic evaluation and optimization of the (Na_2CO_3 + Na_2SO_4 + Na_2S + K_2CO_3 + K_2SO_4 + K_2S) system," *Journal of Chemical Thermodynamics*, vol. 39, no. 6, pp. 942-960, 2007.
- [41] D. Lindberg, R. Backman, and P. Chartrand, "Thermodynamic evaluation and optimization of the (NaCl + Na_2SO_4 + Na_2CO_3 + KCl + K_2SO_4 + K_2CO_3) system," *Journal of Chemical Thermodynamics*, vol. 39, no. 7, pp. 1001-1021, 2007.

- [42] C. W. Bale *et al.*, "FactSage thermochemical software and databases, 2010–2016," *Calphad*, vol. 54, pp. 35-53, 2016, doi: <https://doi.org/10.1016/j.calphad.2016.05.002>.
- [43] D. Lindberg, R. Backman, P. Chartrand, and M. Hupa, "Towards a comprehensive thermodynamic database for ash-forming elements in biomass and waste combustion—Current situation and future developments," *Fuel processing technology*, vol. 105, pp. 129-141, 2013.
- [44] J. Fábry, V. Petricek, P. Vanek, and I. Cisarova, "Phase transition in $K_3Na(MoO_4)_2$ and determination of the twinned structures of $K_3Na(MoO_4)_2$ and $K_{2.5}Na_{1.5}(MoO_4)_2$ at room temperature," *Acta Crystallographica Section B: Structural Science*, vol. 53, no. 4, pp. 596-603, 1997.
- [45] A. D. Pelton, P. Chartrand, and G. Eriksson, "The modified quasi-chemical model: Part IV. Two-sublattice quadruplet approximation," *Metallurgical and Materials Transactions A*, vol. 32, no. 6, pp. 1409-1416, 2001.
- [46] M. Hillert, "The compound energy formalism," *Journal of Alloys and Compounds*, vol. 320, no. 2, pp. 161-176, 2001, doi: [https://doi.org/10.1016/S0925-8388\(00\)01481-X](https://doi.org/10.1016/S0925-8388(00)01481-X).
- [47] M. Hillert, B. Jansson, and B. Sundman, "Application of the Compound-Energy Model to Oxide Systems/ Anwendung des "Compound-Energy"-Modells auf Oxidsysteme," *International Journal of Materials Research*, vol. 79, no. 2, pp. 81-87, 1988, doi: [doi:10.1515/ijmr-1988-790203](https://doi.org/10.1515/ijmr-1988-790203).
- [48] B. Sundman and J. Ågren, "A regular solution model for phases with several components and sublattices, suitable for computer applications," *Journal of physics and chemistry of solids*, vol. 42, no. 4, pp. 297-301, 1981.
- [49] G. Cacciamani, "An introduction to the calphad method and the compound energy formalism (CEF)," *Tecnologia em Metalurgia, Materiais e Mineração*, vol. 13, no. 1, pp. 16-24, 2016.
- [50] K. H. Kumar and P. Wollants, "Some guidelines for thermodynamic optimisation of phase diagrams," *Journal of alloys and compounds*, vol. 320, no. 2, pp. 189-198, 2001.
- [51] V. Ghetta, J. Fouletier, and P. Taxil, *Sels fondus à haute température*. PPUR Presses polytechniques, 2009.
- [52] A. S. Khanna, *Introduction to high temperature oxidation and corrosion*. ASM international, 2002.
- [53] R. A. Rapp and K. S. Goto, "The Hot Corrosion of Metals by Molten Salts," *ECS Proceedings Volumes*, vol. 1981-10, no. 1, p. 159, 1981, doi: [10.1149/198110.0159PV](https://doi.org/10.1149/198110.0159PV).
- [54] P. Hancock, "Vanadic and chloride attack of superalloys," *Materials Science and Technology*, vol. 3, no. 7, pp. 536-544, 1987, doi: [10.1080/02670836.1987.11782265](https://doi.org/10.1080/02670836.1987.11782265).
- [55] E. L. Simons, G. V. Browning, and H. Liebhafsky, "Sodium sulfate in gas turbines," *Corrosion*, vol. 11, no. 12, pp. 17-26, 1955.
- [56] R. Rapp, "Hot corrosion of materials: a fluxing mechanism?," *Corrosion science*, vol. 44, no. 2, pp. 209-221, 2002.

- [57] J. Stringer, "High-temperature corrosion of superalloys," *Corrosion Science and Technology*, vol. 3, no. 7, pp. 482-493, 1987.
- [58] J. R. Nicholls, "Designing oxidation-resistant coatings," *JOM*, vol. 52, no. 1, pp. 28-35, 2000, doi: 10.1007/s11837-000-0112-2.
- [59] F. Armanet, G. Béranger, and G. Moulin, "Corrosion par les gaz à haute température des métaux et alliages réfractaires," 2012.
- [60] P. Steinmetz and C. Rapin, "Corrosion of metallic materials in waste incinerators," in *Materials science forum*, 1997, vol. 251: Trans Tech Publ, pp. 505-518.
- [61] P. Daniel, L. Paul, and J. Barna, "Fire-side corrosion in refuse-fired boilers," *Mater. Performance*, vol. 27, no. 5, 1988.
- [62] D. Lindberg, R. Backman, M. Hupa, and P. Chartrand, "Thermodynamic evaluation and optimization of the (Na+ K+ S) system," *Journal of Chemical Thermodynamics*, vol. 38, no. 7, pp. 900-915, 2006.
- [63] F. Ropital, *Corrosion et dégradation des matériaux métalliques: compréhension des phénomènes et applications dans l'industrie pétrolière et des procédés*. Éd. Technip, 2009.
- [64] F. J. Frandsen, "Utilizing biomass and waste for power production—a decade of contributing to the understanding, interpretation and analysis of deposits and corrosion products," *Fuel*, vol. 84, no. 10, pp. 1277-1294, 2005.
- [65] M. HAZI, "PROCESSUS D'INTERACTION CORROSION / EROSION / DEPOT DANS LES ENCEINTES DE TRAITEMENT THERMIQUE DES DECHETS," in "n°03-0223/1A ", 2006.
- [66] W. Bakker, "The effect of chlorine on mixed oxidation/sulfidation of stainless steels below 600° C," in *Materials science forum*, 1997, vol. 251: Trans Tech Publ, pp. 575-582.
- [67] K. Nakagawa and Y. Matunaga, "Effect of HCl on the corrosion of waterwall tubes in a waste incineration plant," *Mater. High Temp.*, 10.1080/09603409.1997.11689550 vol. 14, no. 3, pp. 245-250, 1997, doi: 10.1080/09603409.1997.11689550.
- [68] N. Otsuka and R. A. Rapp, "Effects of Chromate and Vanadate Anions on the Hot Corrosion of Preoxidized Ni by a Thin Fused Na₂SO₄ Film at 900° C," *Electrochemical Society*, vol. 137, no. 1, pp. 53-60, 1990.
- [69] W. Bakker and J. Stringer, "Mixed oxidant high temperature corrosion in gasifiers and power plants," vol. 14, no. 2, pp. 101-108, 1997.
- [70] Y. Niu, H. Tan, and S. e. Hui, "Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures," *Progress in Energy Combustion Science*, vol. 52, pp. 1-61, 2016.
- [71] S. Srivastava, K. Godiwalla, and M. Banerjee, "Fuel ash corrosion of boiler and superheater tubes," *Materials Science*, vol. 32, no. 4, pp. 835-849, 1997.
- [72] M. Spiegel, P. Biedenkopf, and H.-J. Grabke, "Corrosion of iron base alloys and high alloy steels in the Li₂CO₃-K₂CO₃ eutectic mixture," *Corrosion Science*, vol. 39, no. 7, pp. 1193-1210, 1997.

- [73] T. Nishina, I. Uchida, and J. R. Selman, "Gas electrode reactions in molten carbonate media part v. electrochemical analysis of the oxygen reduction mechanism at a fully immersed gold electrode," *Electrochemical Society*, vol. 141, no. 5, pp. 1191-1198, 1994.
- [74] S. Benalia, C. Robelin, and P. Chartrand, "Development of a Thermodynamic Model for Chromates, Molybdates, Tungstates, and Vanadates Involved in the Corrosion of Steels (Fe, Cr, Ni, Mo, W, and V) at High Temperatures in Atmospheres Containing O–H–S–C–Cl and Alkaline Salts," in *REWAS 2022: Energy Technologies and CO₂ Management (Volume II)*, Cham, F. Tesfaye *et al.*, Eds., 2022: Springer International Publishing, pp. 3-12.
- [75] S. Benalia, F. Tesfaye, D. Lindberg, L. Hupa, P. Chartrand, and C. Robelin, "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 to publication in Journal of Chemical Engineering Science*, 2023.
- [76] S. Benalia, F. Tesfaye, D. Lindberg, L. Hupa, P. Chartrand, and C. Robelin, "Development of 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," *Submitted to publication in Journal of Industrial & Engineering Chemistry Research*, 2023.
- [77] A. D. Pelton, S. Degterov, G. Eriksson, C. Robelin, and Y. Dessureault, "The modified quasichemical model I—binary solutions," *Metallurgical and Materials Transactions B*, vol. 31, no. 4, pp. 651-659, 2000.
- [78] A. D. Pelton and P. Chartrand, "The modified quasi-chemical model: Part II. Multicomponent solutions," *Metallurgical and Materials Transactions A*, vol. 32, no. 6, pp. 1355-1360, 2001.
- [79] M. Hillert, B. Jansson, and B. Sundman, "Application of the Compound-Energy Model to Oxide Systems/Anwendung des „Compound-Energy“-Modells auf Oxidsysteme," *International Journal of Materials Research*, vol. 79, no. 2, pp. 81-87, 1988.
- [80] Y. Bourhis and C. St John, "On the role of refractory elements in the hot corrosion of nickel base alloys," presented at the Electrochemical Society, 1976.
- [81] J. J. Miller, "The Crystal Structure of Anhydrous Sodium Chromate," *Zeitschrift für Kristallographie - Crystalline Materials*, vol. 94, no. 1-6, pp. 131-136, 1936.
- [82] H. Fischmeister, "The system Na₂SO₄–Na₂CrO₄ and the structure of Na₂SO₄ (III)," *Acta Crystallographica*, vol. 7, no. 11, pp. 776-777, 1954.
- [83] A. Niggli, "The space group of Na₂CrO₄," *Acta Crystallographica*, vol. 7, p. 776, 1954.
- [84] A. Goldberg, W. Eysel, T. Halm, A. Goldberg, W. Eysel, and T. Hahn, "Phase diagram and crystallography of the system Na₂CrO₄–K₂CrO₄," *Neues Jahrbuch für Mineralogie-Monatshefte*, vol. H. 6, pp. 241-252, 1973.
- [85] J. Nimmo, "Sodium chromate (II) at 296 K (neutron)," *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, vol. 37, no. 2, pp. 431-433, 1981.

- [86] V. Amirthalangam and K. S. Venkateswarlu, "The thermal expansion and crystallographic phase transformation of sodium chromate(VI)," *Thermochimica Acta*, 10.1016/0040-6031(82)87145-1 vol. 58, no. 1, pp. 107-9, 1982, doi: 10.1016/0040-6031(82)87145-1.
- [87] M. J. Ferrante, J. Stuve, G. Daut, and L. Pankratz, "Low-temperature heat capacities and high-temperature enthalpies of cuprous and cupric sulfides," *Final Report of Investigations Bureau of Mines, Albany, OR. Albany Metallurgy Research Center.*, 1978.
- [88] C. W. Pistorius, "Phase Relations of Some Potassium Compounds to Very High Pressures," *Zeitschrift für Physikalische Chemie*, vol. 35, no. 1_3, pp. 109-121, 1962.
- [89] J. A. McGinnety, "Redetermination of the structures of potassium sulphate and potassium chromate: the effect of electrostatic crystal forces upon observed bond lengths," *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, vol. 28, no. 9, pp. 2845-2852, 1972.
- [90] W. Eysel, "CRYSTAL-CHEMISTRY OF SYSTEM $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-K}_2\text{CrO}_4\text{-Na}_2\text{CrO}_4$ AND OF GLASERITE PHASE," *American Mineralogist*, vol. 58, no. 7-8, pp. 736-747, 1973.
- [91] I. Lindqvist, "Crystal structure studies on anhydrous sodium molybdates and tungstates," *Acta Chemica Scandinavica*, vol. 4, pp. 1066-1074, 1950.
- [92] H. E. Swanson, *Standard X-ray Diffraction Powder Patterns: Data for 46 substances*. National Bureau of Standards, 1962.
- [93] K. D. Singh Mudher, M. Keskar, K. Krishnan, and V. Venugopal, "Thermal and X-ray diffraction studies on Na_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$ and $\text{Na}_2\text{Mo}_4\text{O}_{13}$," *Journal of Alloys and Compounds*, vol. 396, no. 1, pp. 275-279, 2005, doi: <https://doi.org/10.1016/j.jallcom.2004.12.024>.
- [94] C. L. Lima *et al.*, "Temperature-induced phase transformations in Na_2WO_4 and Na_2MoO_4 crystals," *Journal of Raman Spectroscopy*, vol. 42, no. 4, pp. 799-802, 2011.
- [95] K. Bramnik and H. Ehrenberg, "Study of the $\text{Na}_2\text{O-MoO}_3$ System. $\text{Na}_6\text{Mo}_{11}\text{O}_{36}$ — a New Oxide with Anatase-related Structure, and the Crystal Structures of Na_2MoO_4 ," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 630, no. 8-9, pp. 1336-1341, 2004.
- [96] A. D. Fortes, "Crystal structures of spinel-type Na_2MoO_4 and Na_2WO_4 revisited using neutron powder diffraction," *Acta Crystallographica Section E: Crystallographic Communications*, vol. 71, no. 6, pp. 592-596, 2015.
- [97] P. H. Bottelberghs and F. R. van Buren, "Phase relations, dopant effects, structure, and high electrical conductivity in the $\text{Na}_2\text{WO}_4\text{-Na}_2\text{MoO}_4$ system," *Journal of Solid State Chemistry*, vol. 13, no. 3, pp. 182-191, 1975, doi: [https://doi.org/10.1016/0022-4596\(75\)90117-6](https://doi.org/10.1016/0022-4596(75)90117-6).
- [98] B. Gatehouse and P. Leverett, "Crystal structure of potassium molybdate, K_2MoO_4 ," *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, pp. 849-854, 1969.
- [99] F. Kools, A. Koster, and G. Rieck, "The structures of potassium, rubidium and caesium molybdate and tungstate," *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, vol. 26, no. 12, pp. 1974-1977, 1970.
- [100] J. Warczewski, "Hysteresis of phase transitions and modulated structures in K_2MoO_4 and K_2WO_4 ," *Phase Transitions: A Multinational Journal*, vol. 1, no. 2, pp. 131-142, 1979.

- [101] K. S. Gavrichiev *et al.*, "A calorimetric study of the thermodynamic properties of potassium molybdate," *Russian Journal of Physical Chemistry A*, 10.1134/S0036024409030017 vol. 83, no. 3, pp. 327-333, 2009, doi: 10.1134/S0036024409030017.
- [102] A. Van Den Berg, H. Overeijnder, and F. Tuinstra, "The average structure of K_2MoO_4 in the incommensurate phase at 633 K," *Acta Crystallographica Section C: Crystal Structure Communications*, vol. 39, no. 6, pp. 678-680, 1983.
- [103] A. Van Den Akker, A. Koster, and G. Rieck, "Structure types of potassium and rubidium molybdate and tungstate at elevated temperatures," *Journal of Applied Crystallography*, vol. 3, no. 5, pp. 389-392, 1970.
- [104] C. W. Pistorius, "Phase diagrams of sodium tungstate and sodium molybdate to 45 kbar," *The Journal of Chemical Physics*, vol. 44, no. 12, pp. 4532-4537, 1966.
- [105] K. Okada, H. Morikawa, F. Marumo, and S. Iwai, "Sodium tungstate," *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, vol. 30, no. 7, pp. 1872-1873, 1974.
- [106] M. Hämmer and H. A. Höpfe, "New Insights into Alkali Metal Tungstates: The High Temperature Polymorphism of Na_2WO_4 , the New Polymorph Li_2WO_4 -V and the Redetermined Crystal Structure of $Li_2W_2O_7$," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 648, no. 10, p. e202100373, 2022.
- [107] H. E. Boeke, "Die Mischkristalle von wasserfreiem Natrium-Sulfat,-Molybdat und -Wolframat," *Zeitschrift Für Anorganische und Allgemeine Chemie*, vol. 50, p. 355, 1906.
- [108] J. B. Austin and R. H. H. Pierce, "The Linear Thermal Expansion of Sodium Tungstate Between 20° and 600°," *The Journal of Chemical Physics*, vol. 3, no. 11, pp. 683-686, 1935, doi: 10.1063/1.1749577.
- [109] J. Wang, J. You, M. Wang, L. Lu, A. A. Sobol, and S. Wan, "In-situ high-temperature Raman spectroscopic studies of the vibrational characteristics and microstructure evolution of sodium tungstate dihydrate crystal during heating and melting," *Journal of Raman Spectroscopy*, vol. 49, no. 10, pp. 1693-1705, 2018.
- [110] K. Okada, H. Morikawa, F. Marumo, and S. Iwai, "Disodium ditungstate," *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, vol. 31, no. 4, pp. 1200-1201, 1975.
- [111] C. Luz-Lima *et al.*, "Temperature-dependent Raman spectroscopy studies of phase transformations in the K_2WO_4 and the $MgMoO_4$ crystals," *Vibrational Spectroscopy*, vol. 65, pp. 58-65, 2013/03/01/ 2013, doi: <https://doi.org/10.1016/j.vibspec.2012.11.016>.
- [112] E. Flach, "Kaliumchromat und Natriumchromat, ihre Fähigkeit zur Mischkristall- und Doppelsalz-Bildung und ihre Beziehungen zu den entsprechenden Sulfaten," *Gressner & Schramm*, 37, 1912.
- [113] C. W. Pistorius, "Phase diagrams of sodium sulfate and sodium chromate to 45 kbar," *The Journal of Chemical Physics*, vol. 43, no. 8, pp. 2895-2898, 1965.
- [114] R. Riccardi and C. Sinistri, "Application of differential thermal analysis to the evaluation of latent heats of transition and fusion," *Ricerca Scientifica, Parte 2: Rendiconti, Sezione A: Abiologica* vol. 8, no. 5, pp. 1026-37, 1965.

- [115] L. Denielou, Y. Fournier, J. Petitet, and C. Tequi, "CALORIMETRIC STUDY OF SODIUM CHROMATE, MOLYBDATE AND TUNGSTATE BETWEEN 400 AND 1550 DEGREES K," in "COMPTES RENDUS HEBDOMADAIRES DES SEANCES DE L ACADEMIE DES SCIENCES SERIE C," 1971, vol. 272.
- [116] L. Doyen and R. Frech, "Structure and vibrational dynamics of sodium sulfate/sodium chromate solid solutions," *The Journal of chemical physics*, vol. 104, no. 20, pp. 7847-7853, 1996.
- [117] I. S. Rasninskaya and A. G. Bergman, "Melting-point diagram of the system NaF-NaCl-Na₂CrO₄," *Doklady Akademii Nauk SSSR*, vol. 38, pp. 238-40, 1943.
- [118] Y. Vilnyanski and O. Pudovkina, "The chemistry of the production of sodium chromate," *Journal of Applied Chemistry. USSR*, vol. 20, p. 794, 1947.
- [119] W. H. Hartford, "Properties of technically important hexavalent chromium compounds," *Industrial & Engineering Chemistry*, vol. 41, no. 9, pp. 1993-1997, 1949.
- [120] O. Schmitz-Dumont and A. Weeg, "The influence of the cation radius on the energy of formation of addition compounds. III. The systems alkali fluoride-alkali chromate, molybdate, and tungstate," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 265, pp. 139-55, 1951.
- [121] Z. A. Mateiko and G. A. Bukhalova, "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," *Zhurnal Neorganicheskoi Khimii*, vol. 4, pp. 2329-34, 1959.
- [122] A. Stingle, "Melting point and phase diagram determination with a new precision high-temperature microscope technique," Int. At. Energy Agency, 1968.
- [123] A. G. Bergman and A. S. Sanzharov, "Phase diagrams of systems of sodium and potassium chromates and tungstates," *Ukrainian Chemistry Journal*, vol. 35, no. 12, p. 1328, 1969.
- [124] Y. Shinata, "Accelerated oxidation rate of chromium induced by sodium chloride," *Oxidation of Metals*, vol. 27, no. 5-6, pp. 315-332, 1987.
- [125] V. Tathavadar, M. Antony, and A. Jha, "DETERMINATION OF THE FREE ENERGIES OF FORMATION OF Na₂Cr₂O₄ AND Na₂CrO₄ USING THE SODIUM-beta"-Al₂O₃ SOLID ELECTROLYTE," in *LIGHT METALS-WARRENDALE-PROCEEDINGS-*, 2002: TMS, pp. 31-36.
- [126] T. Nelson, C. Moss, and L. G. Hepler, "Thermochemistry of potassium permanganate, potassium molybdate, potassium chlorate, sodium chlorate, sodium chromate, and sodium dichromate," *Journal of Physical Chemistry*, 10.1021/j100832a507 vol. 64, pp. 376-7, 1960, doi: 10.1021/j100832a507.
- [127] I. Barin, *Thermochemical Data of Pure Substances* (no. Copyright (C) 2018 American Chemical Society (ACS). All Rights Reserved.). VCH, 1989, p. 1829 pp.
- [128] J. E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton, "Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Materials Database (OQMD)," *The Minerals, Metals & Materials Society*, vol. 65, no. 11, pp. 1501-1509, 2013, doi: 10.1007/s11837-013-0755-4.

- [129] S. Kirklin *et al.*, "The Open Quantum Materials Database (OQMD): assessing the accuracy of DFT formation energies," *npj Computational Materials*, vol. 1, no. 1, p. 15010, 2015, doi: 10.1038/npjcompumats.2015.10.
- [130] A. Jain *et al.*, "Commentary: The Materials Project: A materials genome approach to accelerating materials innovation," *APL Materials*, vol. 1, no. 1, p. 011002, 2013, doi: 10.1063/1.4812323.
- [131] E. Groschuff, "Das Verhalten der Kaliumchromate bei höherer Temperatur," *Zeitschrift für anorganische Chemie*, vol. 58, no. 1, pp. 102-112, 1908.
- [132] S. Žemczužny, "Die Schmelzen von Kaliumchlorid mit Silberchlorid und den Kaliumchromaten," *Zeitschrift für anorganische Chemie*, vol. 57, no. 1, pp. 267-277, 1908.
- [133] M. Amadori, "The Relative Behavior of Alkali Sulfates, Chromates, Molybdates and Tungstates at High and Low Temperatures. III," *Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti*, vol. 22, no. I, pp. 609-16, 1913.
- [134] A. Hare, "XLIV. Some cases of polymorphic transformation energies," *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, vol. 48, no. 285, pp. 412-21, 1924.
- [135] D. F. Smith and F. A. Hartgen, "The melting point of potassium chromate," *Fuel in Science and Practice*, vol. 8, p. 302, 1929.
- [136] E. P. Dergunov and A. G. Bergman, "Irreversibly reciprocal systems of sodium and potassium fluorides and chromates," *Izvestiya Sektora Fiziko-Khimicheskogo Analiza, Institut Obshchei i Neorganicheskoi Khimii, Akademiya Nauk S.S.S.R.*, vol. 21, pp. 184-98, 1952.
- [137] E. Lax, *Taschenbuch fuer Chemiker und Physiker-Bd. 1: Makroskopische physikalisch-chemische Eigenschaften* (Berlin: J. Springer, 1967, 3. neu bearb. Aufl.). 1967.
- [138] C. W. F. T. Pistorius and E. Rapoport, "Polymorphism of potassium sulfate, selenate, and chromate to 40 kbar," *Journal of Physics and Chemistry of Solids*, 10.1016/0022-3697(69)90353-9 vol. 30, no. 1, pp. 195-201, 1969, doi: 10.1016/0022-3697(69)90353-9.
- [139] M. Natarajan and E. A. Secco, "Anisotropic conductivity and phase transformation studies in potassium chromate crystals," *Canadian journal of chemistry*, vol. 52, no. 13, pp. 2436-2438, 1974.
- [140] D. Sirousse-Zia, "Etude de propriétés thermodynamiques du chromate de potassium," *Thermochimica Acta*, vol. 19, no. 2, pp. 244-246, 1977.
- [141] K. Kostyrko, M. Skoczylas, and A. Klee, "Certified reference materials for thermal analysis," *Journal of thermal analysis*, vol. 33, no. 1, pp. 351-357, 1988.
- [142] G. Janz and J. Slowick, "Investigations of CsCl, K₂SO₄, and K₂CrO₄ as high temperature calibrants for differential scanning calorimetry," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 586, no. 1, pp. 166-174, 1990.
- [143] B.-K. Choi, "Phase transitions of crystals," *Journal of Physics: Condensed Matter*, vol. 11, no. 3, p. 713, 1999.

- [144] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. XI. Te, Cr, Mo, W* (no. Copyright (C) 2018 American Chemical Society (ACS). All Rights Reserved.). Longmans, Green & Co.
- [145] A. Bergman and O. Vartbaronov, "NEOBRATIMO-VZAIMNAYA SISTEMA IZ KHROMATOV I METABORATOV NATRIYA I KALIYA," *Zhurnal Neorganicheskoi Khimii*, vol. 2, no. 11, pp. 2641-2648, 1957.
- [146] G. Nolte and E. Kordes, "Kryometrische Untersuchungen an geschmolzenen Alkaliwolframaten. I. Bestimmung der Schmelzenthalpien," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 371, no. 3-4, pp. 149-155, 1969.
- [147] A. G. Bergman and A. S. Sanzharov, "Na//SO₄, CO₃, WO₄ system," *Zhurnal Neorganicheskoi Khimii*, vol. 14, no. 9, pp. 2588-9, 1969.
- [148] G. Bukhalova and Z. Topshino, "Li, K= Cl, CrO₄, Li, K= Br, CrO₄ SYSTEMS," *Zhurnal Neorganicheskoi Khimii*, vol. 18, no. 5, pp. 1375-1378, 1973.
- [149] D. D. Wagman *et al.*, "Erratum: The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in SI units [J. Phys. Chem. Ref. Data 11, Suppl. 2 (1982)]," *Journal of Physical and Chemical Reference Data*, vol. 18, no. 4, pp. 1807-1812, 1989.
- [150] M. Popov and V. Kolesov, "OPREDELENIE ISTINNOI TEPLOEMKOSTI TVERDYKH VESHCHESTV PRI NIZKIKH TEMPERATURAKH," *Zhurnal Obshchei Khimii*, vol. 26, no. 9, pp. 2385-2393, 1956.
- [151] P. Caillet, "Anhydrous sodium or potassium polymolybdates and polytungstates," *Bulletin de la Societe Chimique de France* no. 12, pp. 4750-5, 1967.
- [152] V. S. Iyer, R. Agarwal, K. N. Roy, S. Venkateswaran, V. Venugopal, and D. D. Sood, "Thermal properties of sodium molybdenates (Na₂MoO_{4(s)} and Na₂Mo₂O_{7(s)}) by high-temperature Calvet calorimetry in the temperature range 335 K to 760 K," *The Journal of Chemical Thermodynamics* 10.1016/0021-9614(90)90134-C vol. 22, no. 5, pp. 439-48, 1990, doi: 10.1016/0021-9614(90)90134-C.
- [153] A. V. Khoroshilov, G. A. Sharpataya, K. S. Gavrichev, and M. A. Ryumin, "Phase transformations in sodium molybdate studied by differential scanning calorimetry," *Russian Journal of Inorganic Chemistry*, vol. 57, no. 8, pp. 1123-1127, 2012, doi: 10.1134/S0036023612080074.
- [154] S. Julsrud and O. J. Kleppa, "Thermodynamics of charge-unsymmetrical anion mixtures. II. The liquid systems AF-A₂MoO₄ and AF-A₂WO₄," *Acta Chemica Scandinavica, Series A: Physical and Inorganic Chemistry*, vol. A 35, no. 9, pp. 669-78, 1981.
- [155] G. A. Bukhalova and Z. A. Mateiko, "Complex formation and solid solutions in the adiaagonal reciprocal system of the molybdates and chlorides of sodium and potassium," *Zhurnal Obshchei Khimii*, vol. 25, pp. 851-7, 1955.
- [156] I. N. Belyaev, "Phase diagrams of molybdates and tungstates of alkali metals with lead," *Zhurnal Neorganicheskoi Khimii* vol. 6, pp. 1178-88, 1961.
- [157] G. K. Shurdumov, Z. L. Khakulov, M. V. Mokhosoev, K. A. Kodzokov, and R. M. El'mesova, "Thermal analysis, density, and molar volumes of melts of binary systems of

- sodium and potassium molybdates, tungstates, and carbonates," *Zhurnal Neorganicheskoi Khimii* vol. 29, no. 8, pp. 2096-101, 1984.
- [158] R. P. Tangri, V. Venugopal, and D. K. Bose, "Standard molar enthalpies of formation of sodium molybdates ($\text{Na}_2\text{Mo}_n\text{O}_{3n+1}$ with $n = 1, 2, 3$ or 4) at 298.15 K by solution calorimetry," *Thermochimica Acta*, vol. 198, no. 2, pp. 259-265, 1992, doi: [https://doi.org/10.1016/0040-6031\(92\)85082-7](https://doi.org/10.1016/0040-6031(92)85082-7).
- [159] W. W. Weller and E. G. King, "Low-temperature heat capacities and entropies at 298.15°K. of monomolybdates of sodium, magnesium, and calcium," *Bureau of Mines Report of Investigations*, vol. No. 6147, p. 6 pp., 1963.
- [160] M. F. Koehler, L. B. Pankratz, and R. Barany, "Heats of formation of sodium molybdates and tungstates," *Bureau of Mines Report of Investigations* vol. No. 5973, p. 13 1962.
- [161] K. S. Gavrichiev, N. N. Smirnova, M. A. Ryumin, A. V. Tyurin, V. M. Gurevich, and L. N. Komissarova, "Heat capacity and thermodynamic functions of Na_2MoO_4 in the temperature range 0–300K," *Thermochimica Acta*, vol. 463, no. 1, pp. 41-43, 2007, doi: <https://doi.org/10.1016/j.tca.2007.07.005>.
- [162] A. Zhidikova and O. Kuskov, "Determination of thermodynamic constants of calcium molybdate (powellite) and sodium molybdate," *Geokhimiya*, vol. 9, pp. 1149-1151, 1971.
- [163] H. S. Klooster, "Die Bestimmung der Umwandlungspunkte bei den Sulfaten, Molybdaten und Wolframaten des Natriums und Kaliums," *Zeitschrift für anorganische Chemie* vol. 85, no. 1, pp. 49-64, 1914, doi: <https://doi.org/10.1002/zaac.19140850107>.
- [164] F. Hoermann, "Beitrag zur Kenntnis der Molybdate und Wolframate. Die binären Systeme: $\text{Li}_3\text{MoO}_4\text{-MoO}_3$, $\text{Na}_2\text{MoO}_4\text{-MoO}_3$, $\text{K}_3\text{MoO}_4\text{-MoO}_3$, $\text{Li}_2\text{WO}_4\text{-WO}_3$, $\text{Na}_2\text{WO}_4\text{-WO}_3$, $\text{K}_2\text{WO}_4\text{-WO}_3$, $\text{Li}_2\text{MoO}_4\text{-Na}_2\text{MoO}_4$, $\text{Li}_2\text{WO}_4\text{-Na}_2\text{WO}_4$, $\text{Li}_2\text{MoO}_4\text{-K}_2\text{MoO}_4$," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 177, no. 1, pp. 145-186, 1929.
- [165] H. Isozaki and T. Ozawa, "A Novel Type of Differential Thermogram Revealed in Potassium Molybdate," *Bulletin of the Chemical Society of Japan*, vol. 39, no. 10, pp. 2307-2308, 1966.
- [166] F. Jaeger and H. Van Klooster, "Studies in the field of silicate chemistry. I. On compounds of lithiumoxide and silica," *Koninklijke Nederlandse Akademie van Wetenschappen Proceedings Series B Physical Sciences*, vol. 16, pp. 857-880, 1914.
- [167] R. Goranson and F. Kracek, "An experimental investigation of the effect of pressure on phase equilibria of sodium tungstate and of related thermodynamic properties," *The Journal of Chemical Physics*, vol. 3, no. 2, pp. 87-92, 1935.
- [168] Y. L. Suponitskiy, E. S. Zolotova, A. G. Dyunin, and S. E. Liashenko, "Thermodynamic Properties of M_2EO_4 , $\text{M}_2\text{Mo}_x\text{O}_{3x+1}$ and Double Chromates ($\text{M} = \text{Li, Na, K, Rb, Cs}$; $\text{E} = \text{Cr, Mo, W}$)," *Russian Journal of Physical Chemistry A*, vol. 92, no. 3, pp. 397-400, 2018, doi: 10.1134/S0036024418030299.
- [169] G. A. Bukhalova and Z. A. Mateiko, "The adiaagonal reciprocal system of the chlorides and tungstates of sodium and potassium," *Zhurnal Obshchei Khimii*, vol. 26, pp. 2119-24, 1956.
- [170] M. W. Chase Jr, "NIST-JANAF thermochemical tables," *Journal of Physical and Chemical Reference Data, Monograph*, vol. 9, 1998.

- [171] E. G. King and W. W. Weller, *Low-temperature Heat Capacities and Entropies at 298.150 K. of Monotungstates of Sodium, Magnesium, and Calcium*. US Department of the Interior, Bureau of Mines, 1961.
- [172] V. B. Parker, *Thermal properties of aqueous uni-univalent electrolytes*. US Government Printing Office Washington, DC, 1965.
- [173] J. Sherfey and A. Brenner, "Electrochemical calorimetry," *Journal of the Electrochemical Society*, vol. 105, no. 11, p. 665, 1958.
- [174] R. L. Graham and L. G. Hepler, "Thermochemistry of Sodium Tungstate, Silver Tungstate and Tungstic Acid," *Journal of the American Chemical Society*, vol. 80, no. 14, pp. 3538-3540, 1958.
- [175] F. D. Rossini, F. D. Rossini, W. H. Evans, S. Levine, and I. Jaffe, *Circular of the Bureau of Standards no. 500: Selected Values of Chemical Thermodynamic Properties*. US Department of Commerce, National Institute of Standards and Technology, 1952.
- [176] M. W. Hisham and S. W. Benson, "Thermochemistry of inorganic solids. 8. Empirical relations among the enthalpies of formation of different anionic compounds," *The Journal of Physical Chemistry*, vol. 92, no. 21, pp. 6107-6112, 1988.
- [177] J. H. M. Van Liempt, "Die binären Systeme Na_2SiO_3 - Na_2WO_4 , K_2SiO_3 - K_2WO_4 , und Na_2WO_4 , K_2WO_4 ," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 122, p. 175, 1922.
- [178] A. G. Bergman, A. I. Kislova, and V. L. Posypaiko, "Investigation of ternary systems of chlorides, sulfates, and tungstates of lithium and potassium. II," *Zhurnal Obshchei Khimii*, vol. 25, pp. 9-11, 1955.
- [179] G. A. Bukhalova and Z. A. Mateiko, "The adiaagonal reciprocal system of the chlorides and tungstates of sodium and potassium," *Zhurnal Obshchei Khimii*, vol. 26, pp. 2365-70, 1956.
- [180] J. Küpper and R. A. Rapp, "Oxidation/reduction Reactions of molybdate ions in sodium sulfate at 1200 K," *Materials and Corrosion* vol. 38, no. 11, pp. 674-682, 1987.
- [181] S. Liu, Q. Chen, and P. Zhang, "Thermodynamic properties of $\text{Na}_2\text{W}_2\text{O}_7(\text{s})$ and $\text{Na}_2\text{W}_4\text{O}_{13}(\text{s})$ in the temperature range 298.15-1000 K," *Thermochimica Acta* 10.1016/S0040-6031(00)00761-9 vol. 371, no. 1-2, pp. 7-11, 2001, doi: 10.1016/S0040-6031(00)00761-9.
- [182] N. C. Panagiotopoulos and I. D. Brown, "Crystal structure of α -sodium dichromate(VI) and the α - β phase transition," *Acta Crystallographica Section B*, 10.1107/S056774087300350X vol. 29, no. Pt. 4, pp. 890-4, // 1973, doi: 10.1107/S056774087300350X.
- [183] P. L. Robinson, G. E. Stephenson, and H. V. A. Briscoe, "LXXIX.—A determination of the melting and transition points of potassium dichromate," *Journal of the Chemical Society, Transactions*, vol. 127, pp. 547-549, 1925.
- [184] N. S. Afonskii, "Volatility of sodium and potassium chromates," *Zhurnal Neorganicheskoi Khimii*, vol. 7, pp. 2640-1, 1962.
- [185] R. G. Samuseva, I. F. Poletaev, and V. E. Plyushchev, "Fusion diagrams of the systems $\text{Na}_2\text{Cr}_2\text{O}_7$ - $\text{Rb}_2\text{Cr}_2\text{O}_7$ and $\text{Na}_2\text{Cr}_2\text{O}_7$ - $\text{Cs}_2\text{Cr}_2\text{O}_7$," *Zhurnal Neorganicheskoi Khimii*, vol. 7, pp. 1146-9, 1962.

- [186] Y. I. Vesnin and L. A. Khripin, "Polymorphic transformations of alkali metal bichromates," *Zhurnal Neorganicheskoi Khimii*, vol. 11, no. 10, pp. 2216-21, 1966.
- [187] J. Jaffray and A. Labary, "Polymorphism of potassium dichromate crystals," in "Compt. rend.," 1956, vol. 242.
- [188] G. S. Rao, "SPACE GROUP SYMMETRY OF $K_2Cr_2O_7$," *Journal of the Indian Institute of Science*, vol. 41, no. 3, p. 47, 1959.
- [189] U. Klement and M. Schwab Georg, "Die Modifikationen des Kalium- und Rubidiumdichromates," in *Zeitschrift für Kristallographie - Crystalline Materials* vol. 114, ed, 1960, p. 170.
- [190] E. A. Kuz'min, V. V. Ilyukhin, and N. V. Belov, "Crystal structure of potassium dichromate (lopezite)," *Doklady Akademii Nauk SSSR*, vol. 173, no. 5, pp. 1068-71, 1967.
- [191] J. Brandon and I. Brown, "An accurate determination of the crystal structure of triclinic potassium dichromate, $K_2Cr_2O_7$," *Canadian Journal of Chemistry*, vol. 46, no. 6, pp. 933-941, 1968.
- [192] L. A. Zhukova and Z. G. Pinsker, "Electron diffraction study of the structure of potassium bichromate," *Kristallografiya*, vol. 9, no. 1, pp. 44-9, 1964.
- [193] E. Mitscherlich, "Über die Farbenänderung des Quecksilberjodids durch die Wärme," *Pogg. Ann*, vol. 28, p. 116, 1833.
- [194] G. Saraiva, W. Paraguassu, M. Maczka, P. Freire, F. De Sousa, and J. Mendes Filho, "Temperature-dependent Raman scattering studies on $Na_2Mo_2O_7$ disodium dimolybdate," *Journal of Raman Spectroscopy*, vol. 42, no. 5, pp. 1114-1119, 2011.
- [195] M. Seleborg, "A refinement of the crystal structure of disodium dimolybdate," *Acta Chemica Scandinavica*, vol. 21, no. 2, pp. 499-504, 1967.
- [196] S. A. Magarill and R. F. Klevtsova, "Crystal structure of potassium dimolybdate $K_2Mo_2O_7$," *Kristallografiya*, vol. 16, no. 4, pp. 742-5, 1971.
- [197] K.-J. Range and H. Haase, " $Na_2W_2O_7$ (II), a high-pressure phase of disodium ditungstate (VI)," *Acta Crystallographica Section C: Crystal Structure Communications*, vol. 46, no. 2, pp. 317-318, 1990.
- [198] P. I. Fedorov and M. V. Mokhosev, "Equilibrium diagram of the disodium ditungstate-disodium dimolybdate," *Zhurnal Neorganicheskoi Khimii*, vol. 6, pp. 122-123, 1961.
- [199] P. I. Fedorov and M. V. Mokhosev, "Purification of tungsten compounds from molybdenum admixtures by zone melting," *Razdelenie Blizkikh po Svoistvam Redkikh Metal.*, pp. 224-32, 1962.
- [200] J. L. Holm, "An investigation of the thermochemical properties of the alkali dichromates by DSC," 1980, vol. 2, no. Copyright (C) 2019 American Chemical Society (ACS). All Rights Reserved.: Birkhaeuser, pp. 105-10.
- [201] A. Lehrman, H. Selditch, and P. Skell, "The Binary System Potassium Dichromate—Sodium Dichromate," *Journal of the American Chemical Society*, vol. 58, no. 9, pp. 1612-1615, 1936.

- [202] P. Nguyen-Duy and E. A. Dancy, "Calorimetric determination of the thermodynamic properties of the alkali metal salts NaNO_3 , KNO_3 , $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$ and their binary eutectic solutions," *Thermochimica Acta*, vol. 39, no. 2, pp. 95-102, 1980.
- [203] K. H. Breuer and W. Eysel, "The calorimetric calibration of differential scanning calorimetry cells," *Thermochimica Acta*, vol. 57, no. 3, pp. 317-329, 1982, doi: [https://doi.org/10.1016/0040-6031\(82\)80043-9](https://doi.org/10.1016/0040-6031(82)80043-9).
- [204] I. Dellien, F. Hall, and L. G. Hepler, "Chromium, molybdenum, and tungsten: thermodynamic properties, chemical equilibria, and standard potentials," *Chemical Reviews*, vol. 76, no. 3, pp. 283-310, 1976.
- [205] C. Robelin, P. Chartrand, and A. D. Pelton, "Thermodynamic evaluation and optimization of the $(\text{NaNO}_3+\text{KNO}_3+\text{Na}_2\text{SO}_4+\text{K}_2\text{SO}_4)$ system," *The Journal of Chemical Thermodynamics*, vol. 83, pp. 12-26, 2015, doi: <https://doi.org/10.1016/j.jct.2014.10.024>.
- [206] J. B. Bates, L. M. Toth, A. S. Quist, and G. E. Boyd, "Vibrational spectra of crystalline, molten, and aqueous potassium dichromate," *Spectrochimica Acta Part A*, vol. 29A, no. 8, pp. 1585-600, 1973.
- [207] H. S. Roberts, "Some new standard melting points at high temperatures," *Physical Review*, vol. 23, no. 3, p. 386, 1924.
- [208] M. Hassanein and E. Kordes, "Kryometrische Untersuchungen. III. Über den Molekularzustand einiger Silicate, Phosphate und Sulfate in geschmolzenem $\text{K}_2\text{Cr}_2\text{O}_7$," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 381, no. 3, pp. 241-246, 1971.
- [209] D. P. Nguyen and E. A. Dancy, "The potassium nitrate-potassium dichromate binary phase diagram," *Journal of the American Ceramic Society*, vol. 60, no. 1-2, p. 94, 1977.
- [210] T. Sekiya and H. Okuda, "Growth of Cr_2O_3 crystals by the decomposition of a $\text{K}_2\text{Cr}_2\text{O}_7$ melt," *Journal of Crystal Growth*, vol. 46, no. 3, pp. 410-414, 1979, doi: [https://doi.org/10.1016/0022-0248\(79\)90090-3](https://doi.org/10.1016/0022-0248(79)90090-3).
- [211] Z. Nan, X.-Z. Lan, L.-X. Sun, and Z.-C. Tan, "Thermodynamic investigation of crystalline $\text{K}_2\text{Cr}_2\text{O}_7$ and aqueous $\text{K}_2\text{Cr}_2\text{O}_7$ solution," *International journal of thermal sciences*, vol. 42, no. 7, pp. 657-664, 2003.
- [212] W. W. Weller and K. K. Kelley, "Low-temperature heat capacities and entropies at 298.15°K. of sodium dimolybdate and sodium ditungstate," *Bureau of Mines Report of Investigations*, vol. No. 6191, p. 5 pp., 1963.
- [213] "Thermochemical properties of inorganic substances," O. Knacke, O. Kubaschewski, and K. Hesselmann, Eds., 2nd ed. ed. Berlin Springer-Verlag 1991.
- [214] R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta crystallographica section A: crystal physics, diffraction, theoretical and general crystallography*, vol. 32, no. 5, pp. 751-767, 1976.
- [215] Y. L. Suponitskii, O. P. Proshina, and M. K. Karapet'yants, "Enthalpies of formation of alkali metal polymolybdates," *Zhurnal Fizicheskoi Khimii* vol. 52, no. 11, pp. 2956-8, 1978.
- [216] T. Mathews, D. Krishnamurthy, and T. Gnanasekaran, "An electrochemical investigation of the thermodynamic properties of $\text{Na}_2\text{Mo}_2\text{O}_7$ and Na_2NiO_3 ," *Journal of Nuclear*

- Materials*, vol. 247, pp. 280-284, 1997, doi: [https://doi.org/10.1016/S0022-3115\(97\)00075-5](https://doi.org/10.1016/S0022-3115(97)00075-5).
- [217] Q. Chen, S. Liu, and P. Zhang, "Heat capacity of potassium tungstates $K_2W_nO_{3n+1}$ ($n = 2, 3, 4$) at temperatures from 273 K to 979 K," *The Journal of Chemical Thermodynamics*, vol. 31, no. 4, pp. 513-519, 1999.
- [218] D. S. Kaganyuk and V. V. Trachevskii, "Calculation of the heats of formation of some crystalline compounds of molybdenum and tungsten," *Ukrainian Chemistry Journal (Russ. Ed.)*, vol. 52, no. 11, pp. 1135-8, 1986.
- [219] Y. Li, M. Spiegel, and S. Shimada, "Corrosion behaviour of various model alloys with NaCl–KCl coating," *Materials Chemistry and Physics*, vol. 93, pp. 217-223, 2005, doi: 10.1016/j.matchemphys.2005.03.015.
- [220] A. D. Pelton and P. Chartrand, "Thermodynamic evaluation and optimization of the LiCl–NaCl–KCl–RbCl–CsCl–MgCl₂–CaCl₂ system using the modified quasi-chemical model," *Metallurgical and Materials Transactions A*, vol. 32, no. 6, pp. 1361-1383, 2001, doi: 10.1007/s11661-001-0227-2.
- [221] Y. Dessureault, J. Sangster, and A. D. Pelton, "Coupled Phase Diagram/Thermodynamic Analysis of the Nine Common-Ion Binary Systems Involving the Carbonates and Sulfates of Lithium, Sodium, and Potassium," *Journal of The Electrochemical Society*, vol. 137, no. 9, p. 2941, 1990.
- [222] 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_2042290
- [223] S. R. Hall and B. McMahon, *International tables for crystallography, definition and exchange of crystallographic data*. Springer Science & Business Media, 2005.
- [224] 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1838862
- [225] 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1001365
- [226] 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1401687
- [227] α - $\text{Na}_2\text{Cr}_2\text{O}_7$ ($\text{Na}_2[\text{Cr}_2\text{O}_7]$ 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1100126
- [228] K_2CrO_4 ($\text{K}_2[\text{CrO}_4]$ 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_0377606
- [229] $\text{K}_2\text{Cr}_2\text{O}_7$ ($\text{K}_2[\text{Cr}_2\text{O}_7]$ 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1322711
- [230] A. D. Pelton and Y.-B. Kang, "Modeling short-range ordering in solutions," *International Journal of Materials Research*, vol. 98, no. 10, pp. 907-917, 2007, doi: 10.3139/146.101554.
- [231] G. Lambotte and P. Chartrand, "Thermodynamic optimization of the ($\text{Na}_2\text{O} + \text{SiO}_2 + \text{NaF} + \text{SiF}_4$) reciprocal system using the Modified Quasichemical Model in the Quadruplet Approximation," *Journal of Chemical Thermodynamics*, vol. 43, no. 11, pp. 1678-1699, 2011, doi: 10.1016/j.jct.2011.05.038.
- [232] P. Chartrand, "New thermodynamic models for liquid solutions," Copyright © 2023 American Chemical Society (ACS). All Rights Reserved., 2000.
- [233] P. Chartrand and A. D. Pelton, "Thermodynamic evaluation and optimization of the Li, Na, K, Mg, Ca/F, Cl reciprocal system using the modified quasi-chemical model," *Metallurgical and Materials Transactions A*, vol. 32, no. 6, pp. 1417-1430, 2001, doi: 10.1007/s11661-001-0231-6.
- [234] P. Coursol, A. D. Pelton, P. Chartrand, and M. Zamalloa, "THE CaSO_4 - Na_2SO_4 - CaO PHASE DIAGRAM," *Canadian Metallurgical Quarterly*, vol. 44, no. 4, pp. 537-546, 2005, doi: 10.1179/cmqr.2005.44.4.537.
- [235] L. Jin, D. Lindberg, Y. Tsuchiyama, and C. Robelin, "A thermodynamic model for high temperature corrosion applications: The ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{ZnSO}_4 + \text{PbSO}_4$) system," *Chemical Engineering Science*, vol. 260, p. 117847, 2022, doi: <https://doi.org/10.1016/j.ces.2022.117847>.

- [236] M. Temkin, "Mixtures of fused salts as ionic solutions," *Acta physicochimica URSS*, vol. 20, p. 411, 1945.
- [237] J. M. Sangster and A. D. Pelton, "Phase diagrams and thermodynamic properties of the 70 binary alkali halide systems having common ions," *Journal of Physical and Chemical Reference Data*, vol. 16, pp. 509-561, 1987.
- [238] L. Rycerz, "Practical remarks concerning phase diagrams determination on the basis of differential scanning calorimetry measurements," *Journal of Thermal Analysis and Calorimetry*, vol. 113, no. 1, pp. 231-238, 2013, doi: 10.1007/s10973-013-3097-0.
- [239] O. Sackur, "Fused Salts as Solvents I. Cryoscopic Investigations," *Zeitschrift für Physikalische Chemie*, vol. 78, pp. 550-63, 1912.
- [240] I. S. Rassonskaya and A. G. Bergman, "Melt diagram of the ternary system KF-KCl-K₂CrO₄," *Zhurnal Obshchei Khimii*, vol. 22, pp. 1133-36, 1952.
- [241] I. Rassonskaya and A. Bergman, "Diagonal section of the quaternary reciprocal system of sodium and potassium fluorides, chlorides, and chromates," *Zhurnal Obshchei Khimii*, vol. 23, pp. 14-20, 1953.
- [242] O. Sackur, "Abnormal molecular weights in fused salts," *Zeitschrift fuer Elektrochemie und Angewandte Physikalische Chemie*, vol. 16, pp. 649-654, 1910.
- [243] M. C. Simoes, K. J. Hughes, D. B. Ingham, L. Ma, and M. Pourkashanian, "Estimation of the Thermochemical Radii and Ionic Volumes of Complex Ions," *Inorganic Chemistry*, vol. 56, no. 13, pp. 7566-7573, 2017, doi: 10.1021/acs.inorgchem.7b01205.
- [244] N. S. Kurnakov and S. F. Shemtshushny, "Isomorphous Mixtures of Potassium and Sodium Salts," *Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva* vol. 39, pp. 122-23, 1907.
- [245] A. S. Sanzharov and A. G. Bergman, "Potassium sulfate, chromate, and carbonate ternary system," *Zhurnal Neorganicheskoi Khimii* vol. 14, no. 11, pp. 3179-80, 1969.
- [246] M. Amadori, "The Neutral Behavior of Alkaline Sulfates, Chromates, Molybdates and Tungstates at Low and High Temperatures. II," *Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti*, vol. 22, no. I, pp. 453-9, 1913.
- [247] G. A. Bukhalova and Z. A. Mateiko, "Ternary systems consisting of potassium sulfate, chromate, and tungstate and of potassium molybdate, chromate, and tungstate," *Zhurnal Neorganicheskoi Khimii* vol. 5, pp. 1132-4, 1960.
- [248] L. Chatelier, 1894.
- [249] M. Amadori, "Sulle capacità dei sali sodici e potassici di dare composti e cristalli misti," *Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti*, vol. 72, no. II, pp. 903-932, 1913.
- [250] J. Fabry, T. Brezczewski, and G. Madariaga, "Structure determination of the ferroelastic phase of K₃Na(CrO₄)₂ at 200 and 230 K and the redetermination of its parent phase at 290 K," *Acta Crystallographica Section B: Structural Science*, vol. 50, no. 1, pp. 13-22, 1994.

- [251] G. Madariaga and T. Brezczewski, "Structure and phase transition of $K_3Na(CrO_4)_2$," *Acta Crystallographica Section C: Crystal Structure Communications*, vol. 46, no. 11, pp. 2019-2021, 1990.
- [252] $K_3Na(CrO_4)_2(K_3Na[CrO_4]_2 \text{ rt})$ Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials (https://materials.springer.com/isp/crystallographic/docs/sd_1405944). Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1405944
- [253] K. Okada and J. Osaka, "Structures of potassium sodium sulfate and tripotassium sodium disulfate," *Acta Crystallographica Section B*, vol. B36, no. 4, p. 919, 1980, doi: 10.1107/s0567740880004852.
- [254] H. Flood and A. Muan, "The Acidic and basic properties of oxides. IV. Thermal decomposition of dichromates," *Acta Chemica Scandinavica*, vol. 4, p. 364, 1950, doi: 10.3891/acta.chem.scand.04-0364.
- [255] A. P. Palkin and I. M. Bokhovkin, "Double decomposition in the absence of solvents. The irreversible reciprocal system $Na_2Cr_2O_7 + 2KNO_3 \rightleftharpoons K_2Cr_2O_7 + 2NaNO_3$," *Acta Univ. Voronegiensis*, vol. 9, no. No. 3, pp. 5-20(in German 19), // 1937.
- [256] N. Voskresenskaya, N. Evseeva, S. Berul, and I. Vereshchetina, "Handbook of Solid-Liquid Equilibria in Systems of Anhydrous Inorganic Salts : Binary systems," *J Nauk SSSR, Moscow-Leningrad*, vol. 1, 1961.
- [257] A. G. Bergman and A. S. Sanzharov, "The Na // CO_3 , SO_4 , CrO_4 system," *Ukrainian Chemistry Journal*, vol. 36, no. 4, pp. 348-9, 1970.
- [258] A. G. Bergman and A. S. Sanzharov, "Sodium carbonate-sodium sulfate-potassium chromate system," *Zhurnal Neorganicheskoi Khimii* vol. 15, no. 2, pp. 583-4, 1970.
- [259] A. G. Bergman and A. S. Trunin, "The Na, K || Cl, CrO_4 system," *Zhurnal Neorganicheskoi Khimii* vol. 12, no. 7, pp. 1966-8, 1967.
- [260] K. Peters, D. Whittle, and J. Stringer, "Oxidation and hot corrosion of nickel-based alloys containing molybdenum," *Corrosion Science*, vol. 16, no. 11, pp. 791-804, 1976.
- [261] $Na_2MoO_4 (Na_2[MoO_4] \text{ rt})$ 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1815021
- [262] $Na_2Mo_2O_7 \text{ rt}$ structural transitions: Datasheet from "PAULING FILE Multinaries Edition – 2022" in SpringerMaterials (https://materials.springer.com/isp/physical-property/docs/ppp_2e7a378246c34f711dc6882c95f111c4). Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan. [Online]. Available: https://materials.springer.com/isp/physical-property/docs/ppp_2e7a378246c34f711dc6882c95f111c4

- [263] $K_2MoO_4(K_2[MoO_4] \text{ rt})$ 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1220174
- [264] $K_2Mo_2O_7$ 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. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1610363
- [265] I. N. Belyaev and A. K. Doroshenko, "Exchange decomposition in the reciprocal system of sodium and silver sulfate and molybdate," *Zhurnal Obshchei Khimii*, vol. 24, pp. 427-32, 1954.
- [266] A. G. Bergman, A. I. Kislova, and E. I. Korobka, "The ternary adiaagonal-belt type reciprocal system of sulfates and molybdates of lithium and potassium," *Zhurnal Obshchei Khimii*, vol. 24, pp. 1127-35, 1954.
- [267] Z. A. Mateiko and G. A. Bukhalova, "Quaternary system K_2SO_4 - K_2CrO_4 - K_2MoO_4 - K_2WO_4 ," *Zhurnal Neorganicheskoi Khimii*, vol. 5, pp. 2071-5, 1960.
- [268] I. N. Belyaev and M. L. Sholokhovich, "Complex formation and exchange decomposition in the reciprocal system of the pyrophosphates and molybdates of sodium and potassium," *Zhurnal Obshchei Khimii*, vol. 23, pp. 1265-73, 1953.
- [269] Y. Ding, N. Hou, N. Chen, and Y. Xia, "Phase diagrams of Li_2MoO_4 - Na_2MoO_4 and Na_2MoO_4 - K_2MoO_4 systems," *Rare Metals*, vol. 25, no. 4, pp. 316-320, 2006, doi: [https://doi.org/10.1016/S1001-0521\(06\)60060-0](https://doi.org/10.1016/S1001-0521(06)60060-0).
- [270] P. Chartrand and A. D. Pelton, "A predictive thermodynamic model for the Al-NaF-AlF₃-CaF₂-Al₂O₃ system," *Light Met. (Warrendale, PA, U. S.)*, pp. 245-252, 2002.
- [271] E. Groschuff, "Über Wasserfreie Molybdate I," *Zeitschrift für anorganische Chemie*, vol. 58, no. 1, pp. 113-119, 1908, doi: <https://doi.org/10.1002/zaac.19080580112>.
- [272] P. I. Fedorov and M. V. Mokhosoiev, "Reaction of sodium carbonate with disodium ditungstate and dimolybdate," *Zhurnal Neorganicheskoi Khimii*, vol. 6, pp. 123-124, 1961.
- [273] M. Amadori, "Analisi termica dei polimolibdati e poliwolframati di potassio," *Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti*, vol. 72, pp. 893-902, 1913.

ANNEXE A ARTICLE DE CONFÉRENCE REWAS 2022

Development of a Thermodynamic Model for Chromates, Molybdates, Tungstates, and Vanadates Involved in the Corrosion of Steels (Fe, Cr, Ni, Mo, W, and V) at High Temperatures in Atmospheres Containing O–H–S–C–Cl and Alkaline Salts

Sara Benalia, Christian Robelin, and Patrice Chartrand

Published in REWAS 2022: Energy Technologies and CO₂ Management (Volume II)
on February 10, 2022

Abstract This research work falls under the generic theme of modeling high-temperature processes, during energy conversion, flaking, and corrosion phenomenon, for systems converting mainly organic matter into energy. Energy conversion facilities are made of a metal alloy of the type Fe–Cr–Ni–V–Mo–W and are exposed to gaseous species from combustion, or from the flying of ashes. Under certain conditions, highly corrosive molten salts may be formed, causing the protective oxide layer of the steel to be transformed into either chromates, molybdates, tungstates or vanadates, or their mixture. This is called “catastrophic” corrosion. The presence of ash deposits limits the maximum operating temperature and the energy efficiency of the process. Thus, this research aims to develop a thermodynamic model including chromates, molybdates, tungstates, and vanadates that may form in environments containing O–H–S–C–Cl and alkaline salts, to predict the limiting conditions at which ash deposition and corrosion can occur.

Keywords Thermodynamic modeling; Energy conversion processes; Molten salts; Alkaline salts

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Introduction

In this context, our research focuses on the high-temperature modeling of “hot corrosion” products (600–950 °C) in combustion energy conversion processes. This phenomenon occurs most often in combustion furnaces, coal gasification, or biomass conversion units and recovery boilers. The major challenge for manufacturers is to maximize the energy efficiency of these processes [1–12].

To do this, the fuel should be burned with excess oxygen under conditions of high steam pressure and temperature. On the other hand, this trend, which targets such operating conditions, accelerates the risk of corrosion, which consequently limits energy efficiency gains [1–12].

Hot corrosion manifests itself specifically on the coldest parts of installations, where the water vapor circulating under pressure is heated by heat exchange with combustion gases such as furnace walls, tubes of parts of thermal power plants, and steam generators [13].

Environmental corrosiveness is largely related to the amount of air that must be available for combustion and the nature of the fuel used containing impurities (S, Cl, Na, K, V, Zn, Pb, etc.), thus determining the compositions of gases and ashes [12, 14–16]. High-temperature corrosion is usually the result of a combination of oxidation and sulfuration. Indeed, fly ash or alkaline salts can adhere to the metal walls, thus forming deposits.

This results in a change in the chemical potential of the environment at its interface with the metal. Due to the contact of oxygen and sulfur, the deposit has the effect of decreasing the oxygen potential and increasing the sulfur potential, which will prevent the formation of a protective and durable oxide layer [12]. The formation of these types of deposits, often rich in salts, increases the risk of corrosion and even more so when they become liquid, since they can dissolve the protective oxides and attack the metal surface.

Case Study of a Corrosion Problem in the Manufacture of Pulp by the Kraft Process

Figure 1 shows a representative case of corrosion that occurs during pulp manufacturing, mainly at the recovery boiler. This corrosion phenomenon is due to either molten salts or corrosive gases

[9]. Figure 1 includes the main reactions that occur in a recovery boiler as well as their location.

The problems caused by corrosion in recovery boilers are complex. Indeed, the burned black liquor regenerates mainly mixtures of the molten salts Na_2CO_3 and Na_2S in the bottom of the furnace on the hearth [17]. The particulate residues during the combustion of the black liquor are mainly mixtures of sodium sulfate, sodium carbonate, and sodium chloride [18].

On the other hand, the reduction of sulfur to sulfide also produces hydrogen sulfide, small amounts of which may escape with the flue gases when the air supply is insufficient or when the air mixing in the furnace is incomplete. Large instantaneous emissions of hydrogen sulfide can occur as a result of deposits falling from the furnace walls [19].

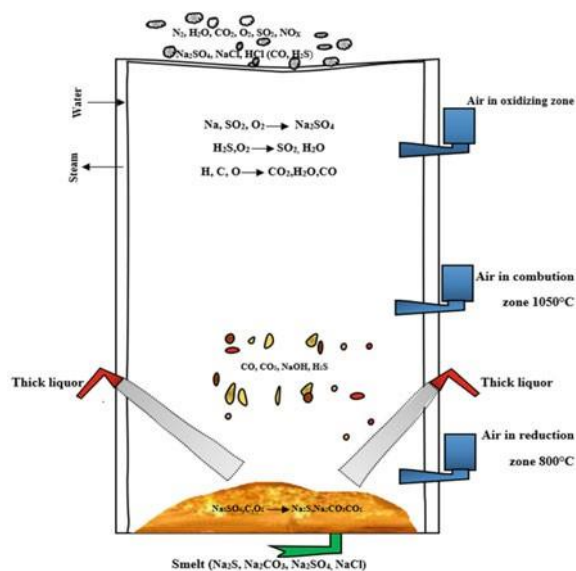


Fig. 1 Chemical reactions in a recovery boiler (inspired from reference [19])

In the upper part of the tubes and in the superheater, corrosion is mainly due to gases containing water vapor, carbon dioxide, oxygen, some hydrogen sulfide H_2S , and sulfur dioxide SO_2 [17]. Sulfur dioxide reacts with sodium in the gas phase to form sodium sulfate.

Since the higher dry matter content of the black liquor leads to an increase in temperature in the furnace, there is a decrease in hydrogen sulfide emissions and an increase in sodium emissions.

The sulfide bound in greater quantities to the sodium sulfate form therefore induces a decrease in the sulfur dioxide emissions [19].

Context of Investigation

The formation of volatile ash and corrosive gases is mainly due to the elements K, Na, Ca, Mg, Fe, Al, Si, P, S, Cl, C, H, and O [14, 15]. These elements, in an incinerating environment, can form complex ionic liquids, molten salts as well as multicomponent gases. A chemical analysis of the solid deposits formed on the heat exchangers revealed the presence mainly of KCl, K_2CO_3 , and K_2SO_4 as well as small amounts of NaCl, Na_2CO_3 , and Na_2SO_4 .

Presently, there are models that can predict the melting properties of K^+ , $Na^+ \parallel Cl^-$, SO_4^{2-} , CO_3^{2-} mixtures with good accuracy [16]. However, thermodynamic models for chromates, molybdates, tungstates, and vanadates are still lacking.

We will focus on developing such models relevant for the corrosion of Fe, Cr, Ni, Mo, W, and V steels in contact with oxygen, hydrogen, sulfur, carbon, chlorine, and alkaline salts (KCl , K_2SO_4 , $NaCl$, Na_2SO_4 , etc.). We will consider the K^+ , $Na^+ \parallel Cl^-$, SO_4^{2-} , CO_3^{2-} , $(CrO_4^{2-}$, $Cr_2O_7^{2-})$, $(MoO_4^{2-}$, $Mo_2O_7^{2-})$, $(WO_4^{2-}$, $W_2O_7^{2-})$, O^{2-} including in particular chromates, molybdates, and tungstates. The two anions VO_4^{2-} and $V_2O_7^{2-}$ related to vanadate-based corrosion will not be included in our model since the corresponding literature on corrosion mechanisms as well as the thermodynamic data required for calibration are extremely limited.

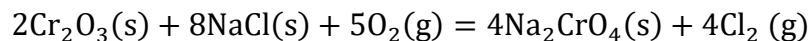
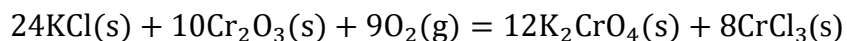
The developed thermodynamic model will permit to predict the boundary conditions under which corrosive deposits can occur and avoid their formation, so as to preserve the facilities, and optimize the energy conversion rate while increasing temperature (reduction of the burned fuel consumption for the same energy efficiency). The main challenge is to avoid the fusion of ash deposits which is favored by higher temperatures.

Corrosion Related to Alloying Elements (Cr, Mo, W, and V)

Chromates

Thermodynamic model of 6+ oxidation state of chromium takes into account the presence of the following compounds: K_2CrO_4 , Na_2CrO_4 , $K_2Cr_2O_7$ and $Na_2Cr_2O_7$. Indeed, the interaction of KCl or NaCl from combustion processes with the protective layer of Cr_2O_3 generates a whole sequence

of corrosion reactions forming K_2CrO_4 and Na_2CrO_4 [7, 10] according to:



During the reaction, chromium oxide converts to sodium chromate (Na_2CrO_4) or potassium chromate, which results in further oxidation of chromium from state III to VI [2]. In addition, the protective oxide will be affected by the emitted chloride, which attacks the steel aggressively [4].

Potassium dichromate ($K_2Cr_2O_7$) is formed as a result of the interaction of KCl with Cr [2]. The latter is involved in the formation of eutectic mixtures with K_2CrO_4 and KCl [2]. The melting temperatures of these mixtures are even lower than the melting points of the pure compounds. Therefore, their presence induces the dissolution of the Cr_2O_3 protective film in the form of chromate or dichromate ions (CrO_4^{2-} or $Cr_2O_7^{2-}$) [2].

Molybdates

Studies by [8, 20] have highlighted the effects of Mo on the hot corrosion of superalloys. The formation of Na_2MoO_4 and a molten mixture of Na_2MoO_4 - MoO_3 causes catastrophic corrosion. The mechanism of the latter remains unclear [21].

Leslie and Fontana [22] investigated the oxidation of Fe-25Ni-16Cr-6Mo (Mo > 3%) nickel-based superalloys at 900 °C and noted that the corrosion of steel had been catastrophic, with a significant accumulation of MoO_3 gas on the metal surface.

Further studies revealed that MoO_3 combines with Na_2SO_4 to produce an acidic SO_2 -rich salt, generating an acidic flux at the deposit/metal interface.

In addition, the evidence of Na_2MoO_4 - MoO_3 and Na_2MoO_4 - $2MoO_4$ liquid solutions, indicates that those exhibit high Cr_2O_3 solubility [8].

Tungstates

Catastrophic corrosion can also originate from Na_2WO_4 [21], which leads to the self-sustained

acidic dissolution of the protective oxide layer when the salt film contains WO_3 (a strongly acidic oxide).

Vanadates

Dissolution of Cr_2O_3 protective layers can occur in the presence of molten vanadium-based deposits. This is because V_2O_5 is a strongly acidic oxide that can promote the automatic dissolution of the protective oxide [9].

Oxides forming acidic solutes of much higher solubility in the presence of vanadates would lead to more rapid attack by molten sulfate-vanadate mixtures than by molten sulfate [10].

Strategy and Description of Our Methodology

Thermodynamic models allow to better investigate the chemistry of ash deposits and heat exchanger alloys, since the combined ash/gas/alloy chemistry controls the melting behaviour of ashes.

For this purpose, a thorough literature review on chromates, molybdates, tungstates, and vanadates was carried out for pure compounds, and binary, ternary, quaternary, and reciprocal (i.e. systems with two or more cations and two or more anions) sub-systems to gather the available data from the literature, and to perform thermodynamic optimizations. We have identified and collected all relevant articles containing experimental data that can be used for the calibration of the thermodynamic model (phase equilibria, heat contents, heat capacities, etc.).

The most reliable data have been identified and selected, and the thermodynamic properties of the following pure compounds have been estimated: Na_2CrO_4 , K_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$, Na_2MoO_4 , K_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_2\text{O}_7$, Na_2WO_4 , K_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, and $\text{K}_2\text{W}_2\text{O}_7$.

The Modified Quasi-Chemical Model in the Quadruplet Approximation [23– 26] is used for the liquid phase; it simultaneously considers the short-range order between first-nearest neighbours (cation/anion) and between second-nearest neighbours (cation/cation and anion/anion). The Compound Energy Formalism (CEF) [27, 28] is used to model the solid solutions. A CALPHAD (CALculation of PHase Diagrams) approach is adopted (see Fig. 2): the model equations allow to describe the Gibbs energy of every phase as a function of temperature and composition.

Predictions can be made for the multicomponent system of interest from the model parameters obtained for the binary sub-systems (and possibly also the ternary and ternary reciprocal sub-systems) using appropriate interpolation techniques. Thermodynamic properties and phase equilibria are calculated using the FactSage thermochemical software, which includes a Gibbs energy minimization algorithm.

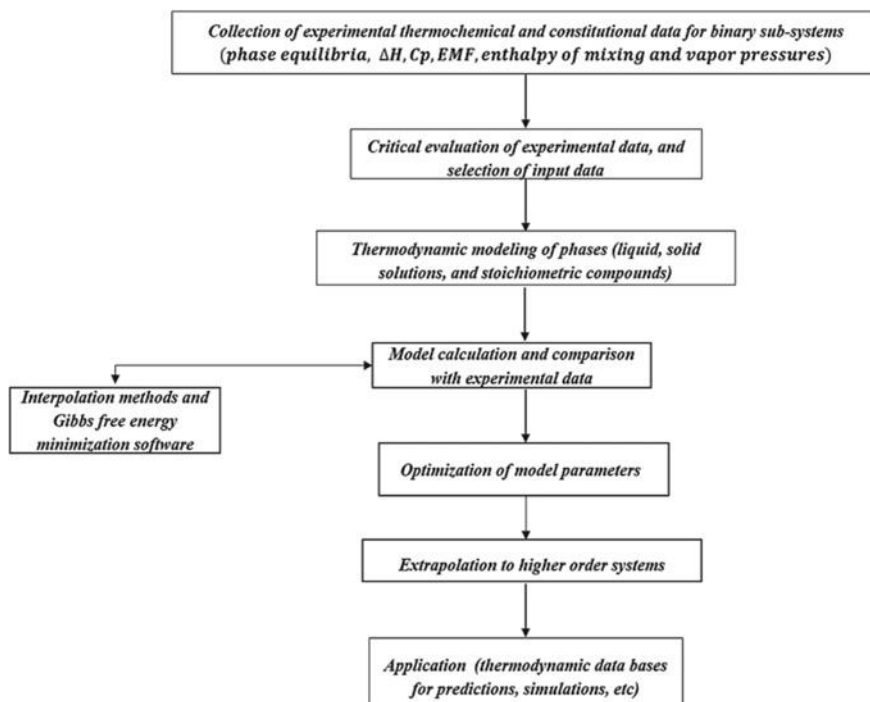


Fig. 2 Flowchart representing the core of the CALPHAD method [29, 30].

For some systems, there are limited or no data available in the literature, or some- times conflicting data. Therefore, additional experiments are required in order to be able to best calibrate the thermodynamic model.

Experiments are in progress at Åbo Akademi Process Chemistry Centre (Turku, Finland) until the end of April 2022. The number of experiments that can be conducted will depend on the restrictions related to the COVID-19 pandemic and on the accessibility of the DSC/DTA apparatuses. XRD and DTA/DSC measurements are being performed for the relevant pure compounds A_2MO_4 and $A_2M_2O_7$ (with $A = Na$ or K , and $M = Cr, Mo, \text{ or } W$). For a given compound, the crystal structures of the various allotropes will be determined by XRD, thus permitting to define properly the various solid solutions (in binary and higher-order systems), and DSC/DTA will permit to measure the temperatures and enthalpies of the solid–solid transitions as well as the temperature and enthalpy

of fusion.

Thereafter, DSC/DTA measurements will be conducted for the relevant binary sub-systems and ternary (common-cation, or ternary reciprocal with Na⁺, K⁺ and 2 different anions) sub-systems. Systems involving chromates, molybdates, or tungstates are being prioritized since reactions of the type $2A_2MO_4 = A_2M_2O_7 + A_2O$ (with A = Na or K, and M = Cr, Mo, or W) are calculated to be very limited. Then, predictions can be made in higher-order sub-systems from the corresponding optimized binary model parameters.

Results

As an example, Fig. 3 shows the calculated Na₂CO₃–Na₂CrO₄ phase diagram along with the available data from the literature. The two compounds Na₂CO₃ and Na₂CrO₄ have several allotropes; the high-temperature forms both have the same crystal structure (hexagonal) with the same space group (P63/mmc) [31, 32].

Thus, the experimental eutectic plateau observed over a wide composition range corresponds to a solid solution miscibility gap (that is, the formation of two solid solutions with the same crystal structure, and different compositions).

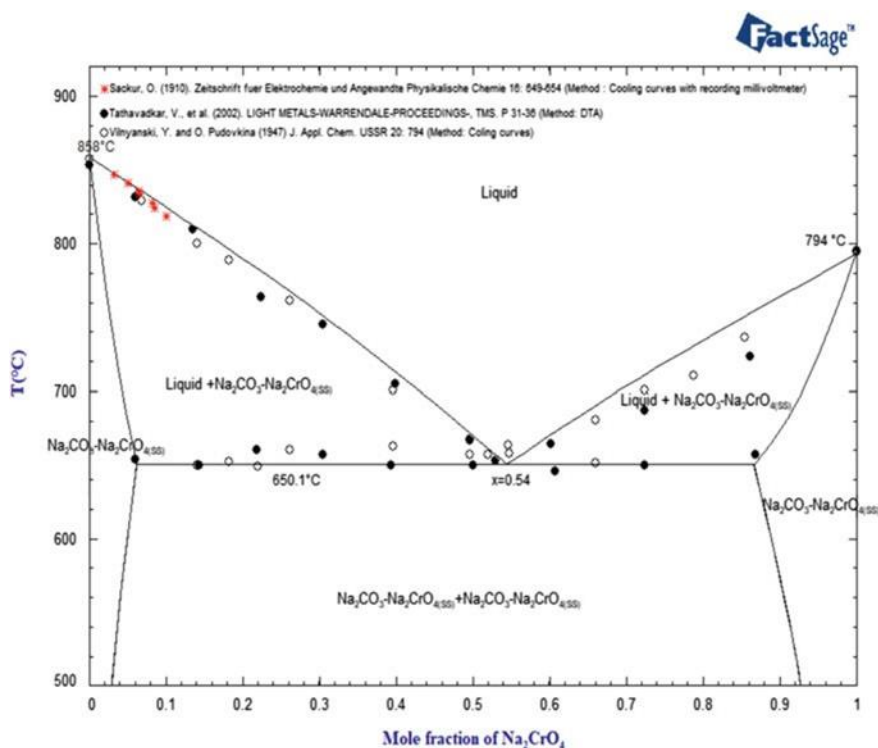


Fig. 3 Calculated Na_2CO_3 - Na_2CrO_4 phase diagram

Summary and Conclusions

The relevance and original contributions of this project consist in the development of a new thermodynamic model applicable to a wide range of problems mentioned previously, in particular, related to combustion energy conversion.

The thermodynamic model developed by including chromates, molybdates, and tungstates will permit researchers to better understand the phenomenon of catastrophic corrosion and avoid the formation of a corrosive liquid phase. Indeed, the predictive capability of the model will be fully employed, allowing to optimize the operating parameters and improve the efficiency (energy and environmental) of various industrial processes.

Additionally, this model will permit to calculate all thermodynamic properties (especially phase equilibria) in every sub-system of the multicomponent system of interest K^+ , $\text{Na}^+ \parallel \text{Cl}^-$, SO_4^{2-} , CO_3^{2-} , $(\text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-})$, $(\text{MoO}_4^{2-}, \text{Mo}_2\text{O}_7^{2-})$, $(\text{WO}_4^{2-}, \text{W}_2\text{O}_7^{2-})$, O^{2-} .

References

1. Paneru M et al (2013) Corrosion mechanism of alloy 310 austenitic steel beneath NaCl deposit under varying SO_2 concentrations in an oxy-fuel combustion atmosphere 27(10):5699–5705
2. Lehmusto J et al (2012) Studies on the partial reactions between potassium chloride and metallic chromium concerning corrosion at elevated temperatures. *Oxid Met* 77(3–4):129–148
3. Goebel J, Pettit F, Goward G (1973) Mechanisms for the hot corrosion of nickel-base alloys. *Met Trans* 4(1):261–278
4. Küpper J, Rapp R (1987) Oxidation/reduction reactions of molybdate ions in sodium sulfate at 1200 K. *Mater Corros* 38(11):674–682
5. Shinata Y (1987) Accelerated oxidation rate of chromium induced by sodium chloride. *Oxid Met* 27(5–6):315–332
6. Lindberg D et al (2006) Thermodynamic evaluation and optimization of the $(\text{Na}^+ \text{K}^+ \text{S})$

system. *J Chem Thermodyn* 38(7):900–915

7. Hazi M (2006) Processus d'interaction corrosion/érosion/dépôt dans les enceintes de traitement thermique des déchets
8. Pettit F et al (1984) Oxidation and hot corrosion of superalloys. *Superalloys* 85:651–687
9. Otsuka N, Rapp RA (1990) Effects of chromate and vanadate anions on the hot corrosion of Preoxidized Ni by a thin fused Na₂SO₄ film at 900° C. *J Electrochem Soc* 137(1):53–60
10. Eliaz N et al (2002) Hot corrosion in gas turbine components. *Eng Fail Anal* 9(1):31–43
11. Stringer and Technology (1987) High-temperature corrosion of superalloys. *Mater Sci Technol* 3(7):482–493
12. Antoni L, Galerie AJ (2003) Corrosion sèche des métaux. Cas industriels: dépôts, milieux fondus 10(M4227):M4227
13. François Armanet GB, Moulin G (2012) Corrosion par les gaz à haute température des métaux et alliages réfractaires. *Technique de l'ingénieur*, no COR378, pp 1–37
14. Huntz A-M, Pieraggi B (2003) Oxydation des matériaux métalliques: comportement à haute température, éd: Hermes-Lavoisier
15. Lacombe P, Dabosi F (1987) Les Ulis, Corrosion des Matériaux à Haute Température
16. Lindberg D (2007) Thermochemistry and melting properties of alkali salt mixtures in black liquor conversion processes. Åbo Akademi University
17. Remeau J-J, H Barthelemy and Techniques (1978) Quelques problèmes de corrosion dans la fabrication de la pâte à papier par le procédé kraft. *Mater Techn* 66(11–12):383–385
18. Lindberg D et al (2013) Towards a comprehensive thermodynamic database for ash-forming elements in biomass and waste combustion—current situation and future developments. *Fuel Process Technol* 105:129–141
19. Pöyry J (1992) Reduction of atmospheric emissions from pulp industry, on behalf of Swedish EPA
20. Fryburg G, Kohl F, Stearns C (1984) Chemical reactions involved in the initiation of hot corrosion of IN-738. *J Electrochem Soc* 131(12):2985–2997

21. Misra A (1986) Mechanism of Na_2SO_4 -induced corrosion of molybdenum containing nickel-base superalloys at high temperatures I: corrosion in atmospheres containing only. *J Electrochem Soc* 133(5):1029–1038
22. Peters K, Whittle D, Stringer J (1976) Oxidation and hot corrosion of nickel-based alloys containing molybdenum. *Corros Sci* 16(11):791–804
23. Pelton AD et al (2000) The modified quasichemical model I—binary solutions. *Metall Mater Trans B* 31(4):651–659
24. Pelton AD, Chartrand P (2001) The modified quasi-chemical model: Part II. multicomponent solutions *Metall Mater Trans A* 32(6):1355–1360
25. Chartrand P, Pelton AD (2001) The modified quasi-chemical model: Part III. two sublattices *Metall Mater Trans A* 32(6):1397–1407
26. Pelton AD, Chartrand P, Eriksson G (2001) The modified quasi-chemical model: Part IV. two-sublattice quadruplet approximation *Metall Mater Trans A* 32(6):1409–1416
27. Hillert M, Jansson B, Sundman B (1988) Application of the compound-energy model to oxide systems/anwendung des compound-energy. Modells auf Oxidsysteme. *Int J Mater Res* 79(2):81–87
28. Sundman B, Ågren J (1981) A regular solution model for phases with several components and sublattices, suitable for computer applications. *J Phys Chem Solids* 42(4):297–301
29. Cacciamani G (2016) An introduction to the calphad method and the compound energy formalism (CEF). *Technol Metal Mater Miner* 13(1):16–24
30. Kumar KH, Wollants P (2001) Some guidelines for thermodynamic optimisation of phase diagrams. *J Alloys Compd* 320(2):189–198
31. Lindberg D, Backman R, Chartrand P (2007) Thermodynamic evaluation and optimization of the ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S} + \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}$) system. *J Chem Thermodyn* 39(6):942–960
32. Goldberg A, et al (1973) Phase diagram and crystallography of the system Na_2CrO_4 – K_2CrO_4 . *N Jb Miner Mh* 241–252

ANNEXE B SUPPORTING INFORMATION (ARTICLE 1)

**CRITICAL EVALUATION AND CALORIMETRIC STUDY OF THE
THERMODYNAMIC PROPERTIES OF Na_2CrO_4 , K_2CrO_4 , Na_2MoO_4 ,
 K_2MoO_4 , Na_2WO_4 , AND K_2WO_4**

DSC thermograms for the compounds K_2CrO_4 , Na_2MoO_4 , K_2MoO_4 , Na_2WO_4 and K_2WO_4 are presented below.

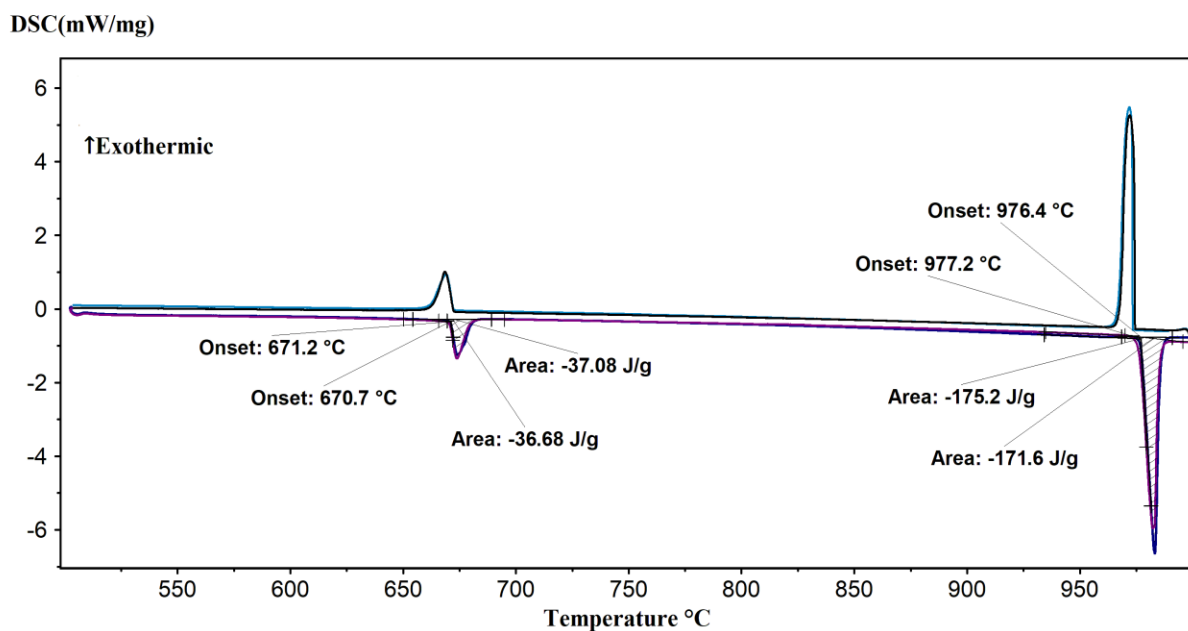


Figure B1 Differential scanning calorimetry (DSC) thermogram for K_2CrO_4 (2nd and 3rd heating/cooling cycles only)

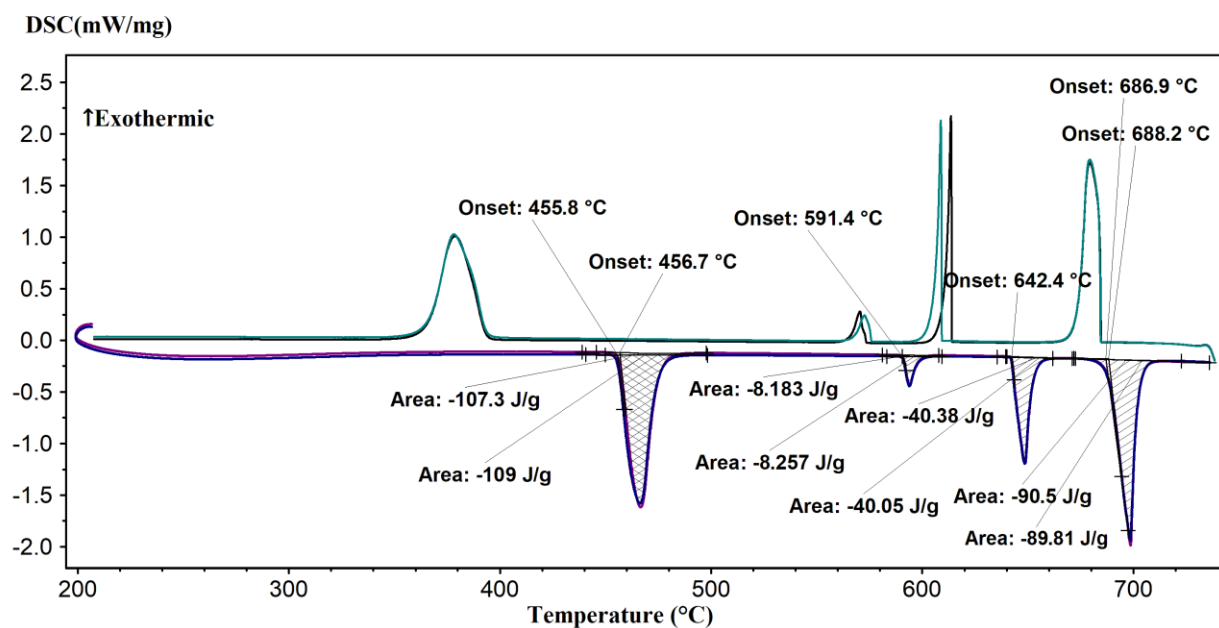


Figure B2 Differential scanning calorimetry (DSC) thermogram for Na_2MoO_4 (2nd and 3rd heating/cooling cycles only)

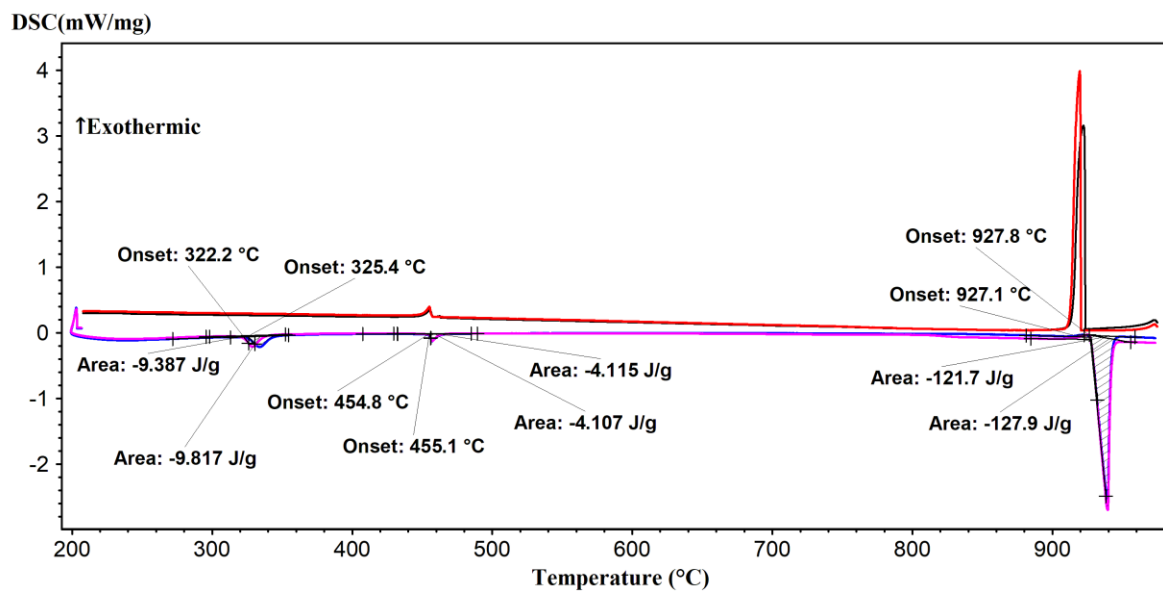


Figure B3 Differential scanning calorimetry (DSC) thermogram for K_2MoO_4 (2nd and 3rd heating/cooling cycles only)

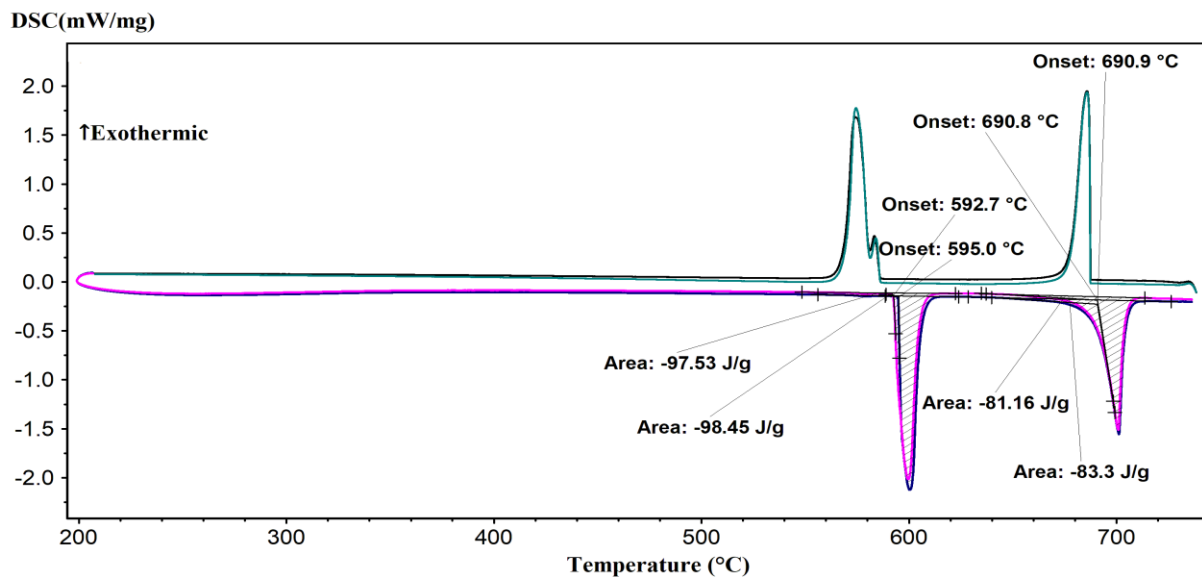


Figure B4 Differential scanning calorimetry (DSC) thermogram for Na₂WO₄ (2nd and 3rd heating/cooling cycles only)

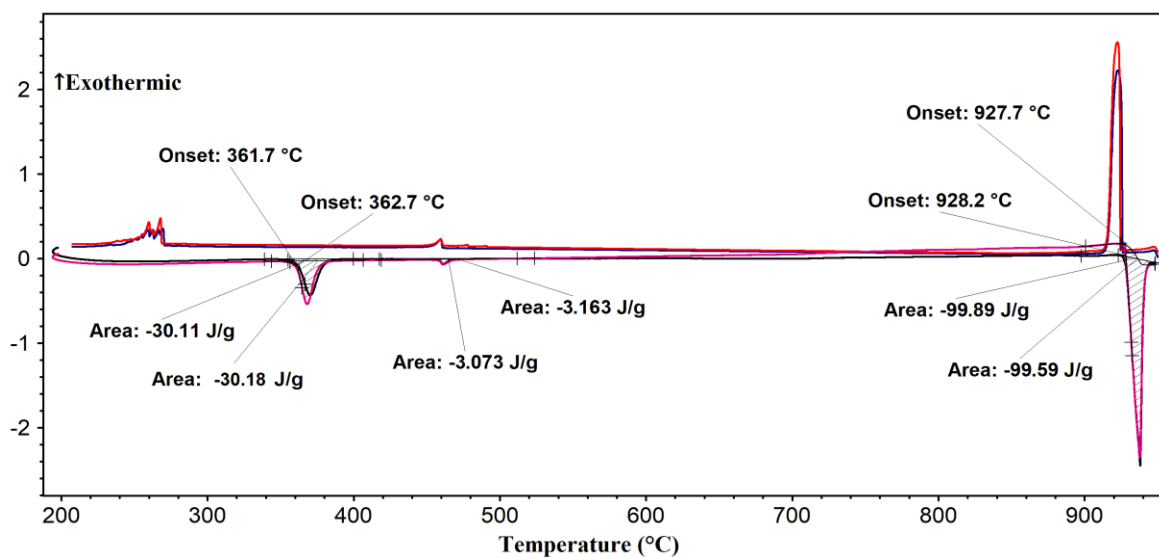


Figure B5 Differential scanning calorimetry (DSC) thermogram for K₂WO₄ (2nd and 3rd heating/cooling cycles only)

ANNEXE C SUPPORTING INFORMATION (ARTICLE 3)

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

Chromate-based common-ion binary sub-systems

DSC-TGA results are presented below for several compositions in the (Na₂CO₃ + Na₂CrO₄), (K₂CO₃ + K₂CrO₄), and (Na₂CrO₄ + K₂CrO₄) common-ion binary sub-systems.

1. The (Na₂CO₃ + Na₂CrO₄) system

Table C1 DSC-TGA results for (Na₂CO₃ + Na₂CrO₄) binary mixtures (2nd and 3rd heating/cooling cycles only)

Mol% of Na ₂ CrO ₄	<i>T</i> _{Onset} (°C) 2 nd heating	<i>T</i> _{Onset} (°C) 3 rd heating	<i>T</i> _{Peak} (°C) 2 nd heating	<i>T</i> _{Peak} (°C) 3 rd heating	Mass Change (%)
5	668.6	668.6	847.0	847.0	-0.24
10	668.9	668.9	829.6	829.6	-0.13
90	343.8	343.8	754.3	754.3	-0.38
92.5	376.0	376.0	774.8	774.9	-0.50
95	379.2	379.6	780.6	780.6	-0.41

2. The (K₂CO₃ + K₂CrO₄) system

Table C2 DSC-TGA results for (K₂CO₃ + K₂CrO₄) binary mixtures (2nd and 3rd heating/cooling cycles only)

Mol% of K ₂ CrO ₄	<i>T</i> _{Onset} (°C) 2 nd heating	<i>T</i> _{Onset} (°C) 3 rd heating	<i>T</i> _{Peak} (°C) 2 nd heating	<i>T</i> _{Peak} (°C) 3 rd heating	Mass Change (%)
40			682.4*	683.6*	-2.07
			826.7	827.5	
60	661.9	662.0	826.3	826.3	-2.39
			861.6	861.6	
80	661.4	661.4	921.0	920.2	-1.27
90	662.5	662.5	947.1	947.5	-0.97

* These temperature values were taken at the maximum of the peak (and not at the onset of the peak) since these were very low intensity peaks.

3. The (Na₂CrO₄ + K₂CrO₄) system

Table C3 DSC-TGA results for mechanical mixtures of pre-treated reagents Na₂CrO₄.4H₂O and K₂CrO₄ in the (Na₂CrO₄ + K₂CrO₄) binary sub-system (2nd and 3rd heating/cooling cycles only)

Mol% of K ₂ CrO ₄	<i>T</i> _{Onset} (°C) 2 nd heating	<i>T</i> _{Onset} (°C) 3 rd heating	<i>T</i> _{Peak} (°C) 2 nd heating	<i>T</i> _{Peak} (°C) 3 rd heating	Mass Change (%)
35	569.0	568.9	232.1*	231.3*	-1.27
			752.9	752.7	
45	537.8	530.6	331.8*	331.5*	1.03**
	597.2	597.5	773.6	772.9	

55	534.1	537.8	330.0*	329.5*	-0.35
	606.6	606.7	802.2	809.0	
65	528.5	533.3	326.3*	327.5*	0.87**
			841.4	843.7	
	590.9	590.9			
70	586.2	586.6	527.5*	528.7*	-0.63
			860.9	860.5	
75	554.1	554.4	278.2*	277.7*	-0.71
			528.2*	528.2*	
			881.4	873.9	

* These temperature values were taken at the maximum of the peak (and not at the onset of the peak) since these were very low intensity peaks.

** There was a small mass gain associated with oxidation due to impurity traces of oxygen in Ar(g).

The binary compositions listed in Table C4 were investigated by DSC-TGA; they were obtained by adding an excess of Na₂CrO₄ or K₂CrO₄ to a sample of chrome-glaserite with the nominal composition of (45 mol% Na₂CrO₄ + 55 mol% K₂CrO₄) equilibrated at 400°C for three weeks.

Table C4 DSC-TGA results for binary mixtures obtained by addition of an excess of Na₂CrO₄ or K₂CrO₄ to an equilibrated sample with the nominal composition (45 mol% Na₂CrO₄ + 55 mol% K₂CrO₄) (1st, 2nd and 3rd heating/cooling cycles only, and all temperatures in °C)

Mol% of K₂CrO₄	T_{Onset} 1st heating	T_{Onset} 2nd heating	T_{Onset} 3rd heating	T_{Peak} 1st heating	T_{Peak} 2nd heating	T_{Peak} 3rd heating	Mass Change (%)
40		601.2	601.1	374.1*	332.3*		-0.35
				497.8*	516.1*	520.6*	
				778.4	779.8	778.4	

65		605.2	605.2	556.7*			-0.31
				809.9	816.4	825.3	
72		599.5	600.3	557.2*			-0.41
				827.8	835.4	836.6	
73	552.5	594.2	594.0	841.0	839.2	841.3	-0.63

* These temperature values were taken at the maximum of the peak (and not at the onset of the peak) since these were very low intensity peaks.

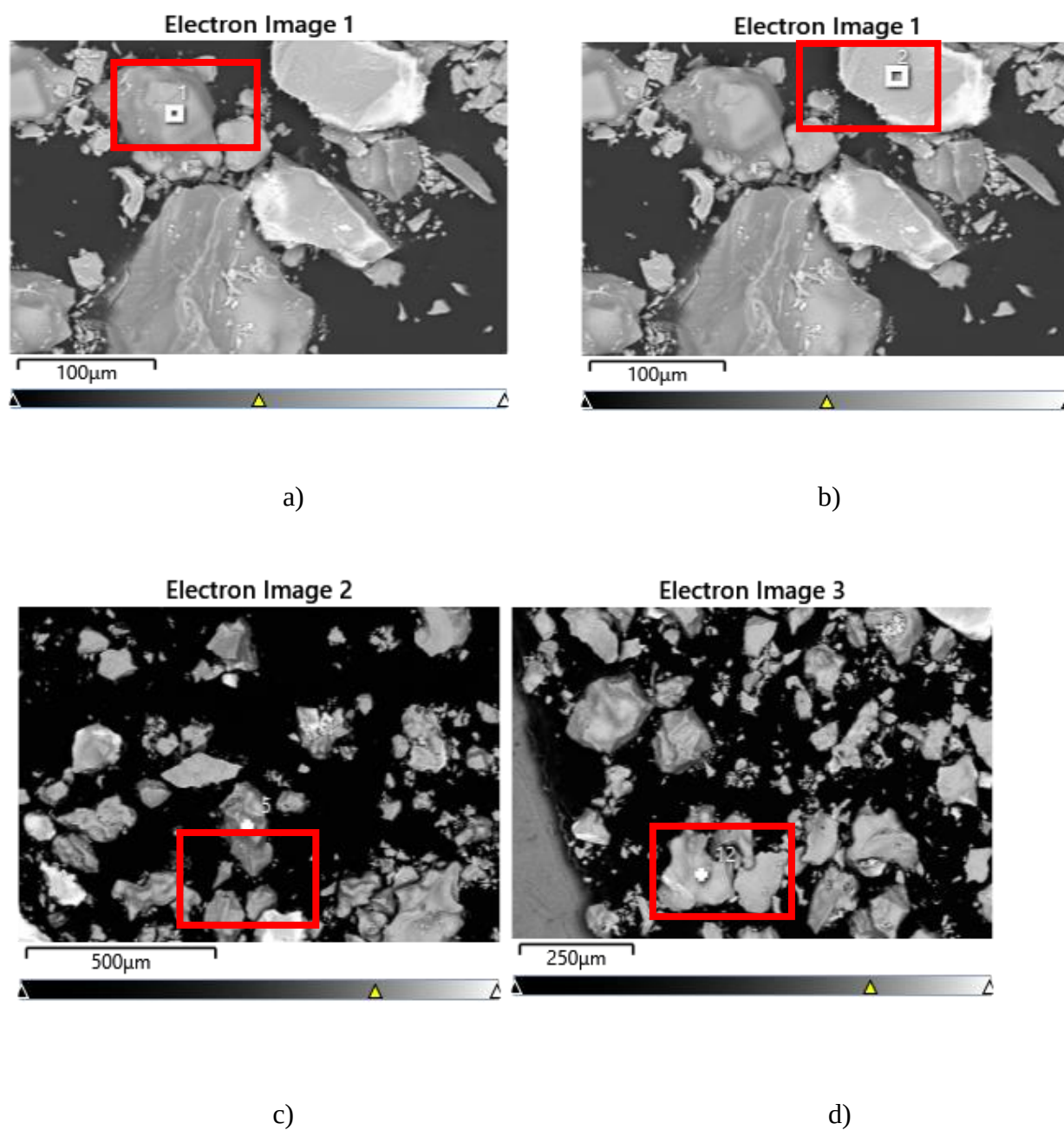


Figure C1 SEM secondary electron images of the equilibrated chrome-glaserite sample with the nominal composition of (45 mol% Na_2CrO_4 + 55 mol% K_2CrO_4) : a) spectrum 1, b) spectrum 2, c) spectrum 5, and d) spectrum 12

Chromate-based common-cation ternary sub-systems

1. The (KCl + K₂CO₃ + K₂CrO₄) system

Table C5 DSC-TGA results for a (KCl + K₂CO₃ + K₂CrO₄) common-cation ternary mixture (2nd and 3rd heating/cooling cycles only)

Composition	T_{Peak} (°C) 2 nd heating	T_{Peak} (°C) 3 rd heating	Mass Change (%)
(55.0 mol% KCl + 28.0 mol% K ₂ CO ₃ + 17.0 mol% K ₂ CrO ₄)	595.5	596.3	-2.34

Chromate-based ternary reciprocal sub-systems

1. The (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) system

Calculations are presented below for four of the fifteen isoplethal sections measured by Bergman and Trunin [1] using the visual-polythermal method. All experimental data (●) were extracted graphically from the smoothed liquidus projection of these authors.

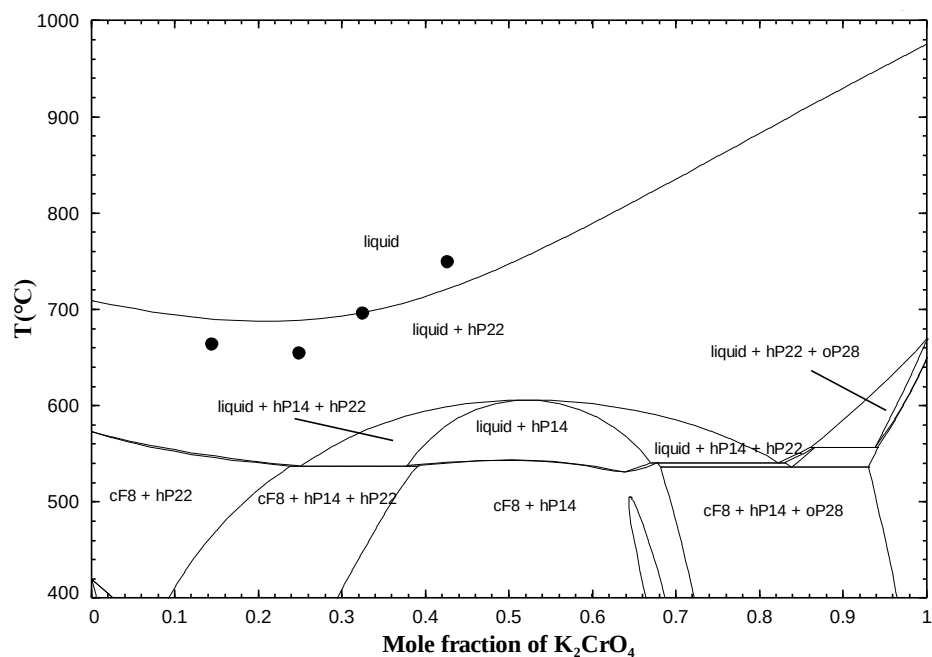


Figure C2 Calculated isoplethal section in the (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) system
 ((Na₂CrO₄)_{0.897}(Na₂Cl₂)_{0.103}-K₂CrO₄, section I)

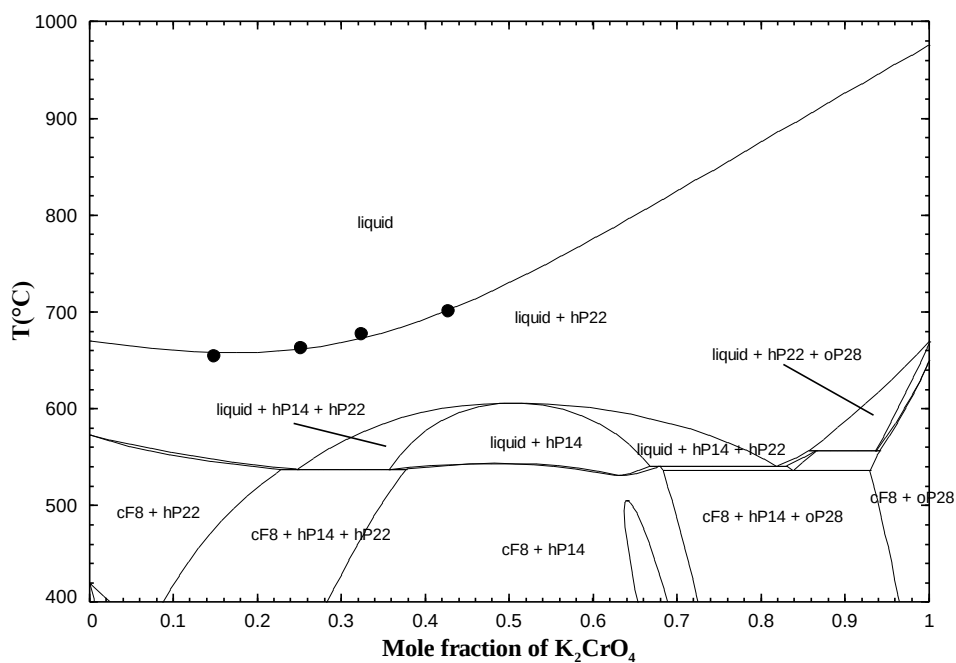


Figure C3 Calculated isoplethal section in the (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) system
 ((Na₂CrO₄)_{0.846}(Na₂Cl₂)_{0.154}-K₂CrO₄, section II)

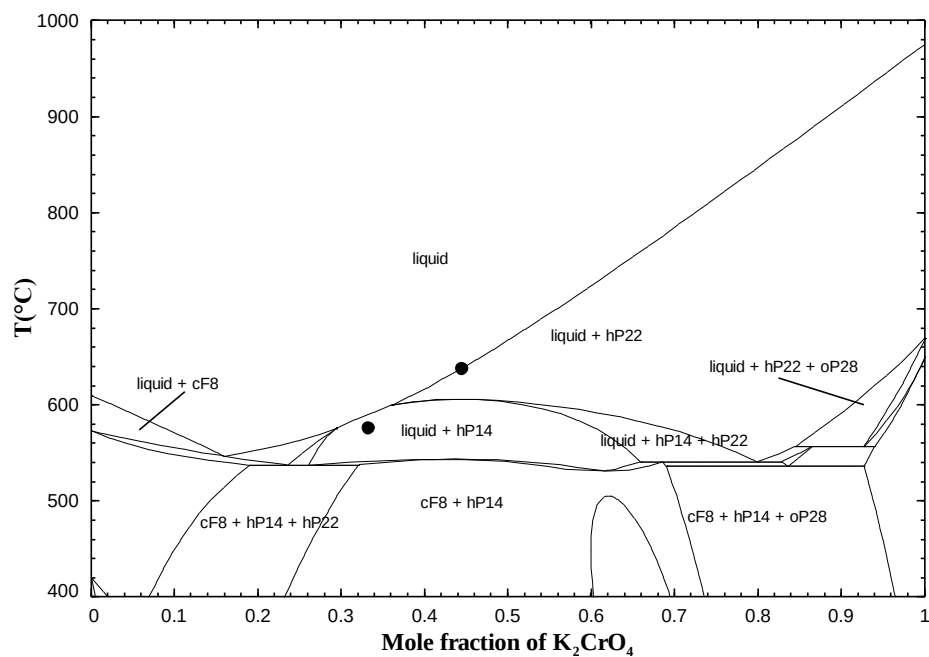


Figure C4 Calculated isoplethal section in the (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) system
 ((Na₂CrO₄)_{0.644}(Na₂Cl₂)_{0.356}-K₂CrO₄, section IV)

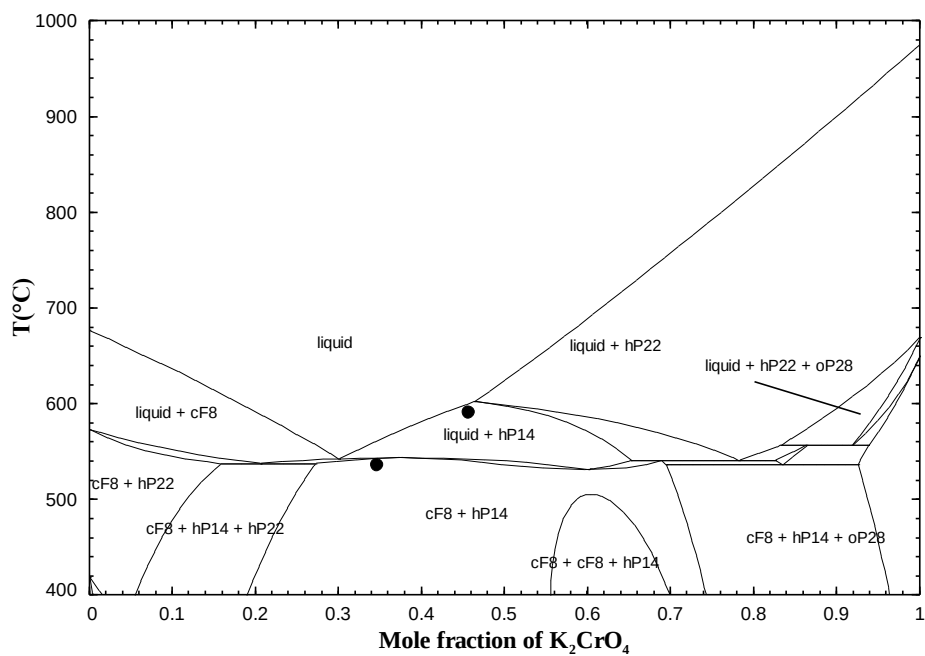


Figure C5 Calculated isoplethal section in the (NaCl + KCl + Na₂CrO₄ + K₂CrO₄) system
 ((Na₂CrO₄)_{0.497}(Na₂Cl₂)_{0.503}-K₂CrO₄, section V)

References

- [1] A. G. Bergman and A. S. Trunin, "The Na, K II Cl, CrO₄ system," *Zhurnal Neorganicheskoi Khimii* vol. 12, no. 7, pp. 1966-8, 1967.

ANNEXE D SUPPORTING INFORMATION (ARTICLE 4)

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

Molybdate-based common-ion binary sub-systems

DSC-TGA results are presented below for various compositions in the (Na₂CO₃ + Na₂MoO₄), (Na₂SO₄ + Na₂MoO₄), (K₂SO₄ + K₂MoO₄), (Na₂CrO₄ + Na₂MoO₄), (K₂CrO₄ + K₂MoO₄), and (Na₂MoO₄ + K₂MoO₄) common-ion binary sub-systems.

4. The (Na₂CO₃ + Na₂MoO₄) system

Table D1 DSC-TGA results for (Na₂CO₃ + Na₂MoO₄) binary mixtures (2nd and 3rd heating/cooling cycles only), in the absence of CO₂ gas

Mol% of Na ₂ MoO ₄	<i>T</i> _{Onset} (°C) 2 nd heating	<i>T</i> _{Onset} (°C) 3 rd heating	<i>T</i> _{Peak} (°C) 2 nd heating	<i>T</i> _{Peak} (°C) 3 rd heating	Mass Change (%)
2.5			393.6*	393.1*	-1.50
			481.6*	482.5*	
			844.9	840.3	
12.7	485.1	488.9	806.4	801.6	-0.78
	514.3	525.1			
22	454.5	455.6	770.0	766.4	-0.95
	488.0	488.1			
	545.4	553.5			
90	453.8	453.8	642.2	642.3	-1.35
	485.2	485.2			

	537.2	547.9			
	595.5	595.6			
95	452.8	453.1	668.9	667.2	-1.09
	485.0	484.7			
	594.4	593.8			
	640.9	640.7			

* These temperature values were taken at the maximum of the peak (and not at the onset of the peak) since these were very low intensity peaks.

Table D2 DSC-TGA results for ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{MoO}_4$) binary mixtures (2nd and 3rd heating/cooling cycles only), in the presence of CO_2 gas

Mol% of Na ₂ MoO ₄	T _{Onset} (°C) 2 nd heating	T _{Onset} (°C) 3 rd heating	T _{Peak} (°C) 2 nd heating	T _{Peak} (°C) 3 rd heating	Mass Change (%)
22	465.8	466.4	786.4	788.6	-0.62
	547.4	547.4			
	594.9	594.9			
50	464.2	463.6	601.4	601.4	-0.43
	574.6	574.6			
	594.8	594.8			
85	461.2	461.9	646.6	646.6	-0.11
	575.7	575.7			
	594.9	595.0			

* Since the liquidus temperature was not observed during the 2nd and 3rd heating cycles, these two values were taken from the 2nd and 3rd cooling cycles, respectively.

5. The ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$) system

Table D3 DSC-TGA results for ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$) binary mixtures (2nd and 3rd heating/cooling cycles only)

Mol% of Na ₂ MoO ₄	T _{Onset} (°C) 2 nd heating	T _{Onset} (°C) 3 rd heating	T _{Peak} (°C) 2 nd heating	T _{Peak} (°C) 3 rd heating	Mass Change (%)
90	591.6	591.6	684.0	684.0	0.29**
92	596.7	596.7	684.9	684.9	0.44**
95	608.6	608.6	686.6	686.6	0.28**
98			172.0*	172.0*	0.16**
	362.0	362.0	688.5	688.5	
	610.7	610.7			
	628.1	628.1			
99	366.0	366.0	689.1	689.1	0.08**
	600.5	600.5			
	634.3	634.3			

* These temperature values were taken at the maximum of the peak (and not at the onset of the peak) since these were very low intensity peaks.

** There was a small mass gain associated with oxidation due to impurity traces of oxygen in $\text{N}_2(\text{g})$.

6. The ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$) system

Table D4 DSC-TGA results for ($\text{K}_2\text{SO}_4 + \text{K}_2\text{MoO}_4$) binary mixtures (2nd and 3rd heating/cooling cycles only)

Mol% of K_2MoO_4	$T_{\text{Onset}} (^{\circ}\text{C})$ 2 nd heating	$T_{\text{Onset}} (^{\circ}\text{C})$ 3 rd heating	$T_{\text{Peak}} (^{\circ}\text{C})$ 2 nd heating	$T_{\text{Peak}} (^{\circ}\text{C})$ 3 rd heating	Mass Change (%)
60	428.3	430.6	915.2	916.4	-0.28
80			394.8*	394.8*	0.03**
			924.4	924.4	

95	441.6	441.6	917.7	917.7	-0.08

* These temperature values were taken at the maximum of the peak (and not at the onset of the peak) since these were very low intensity peaks.

** There was a small mass gain associated with oxidation due to impurity traces of oxygen in Ar(g).

Table D5 DSC-TGA** results for (K₂SO₄ + K₂MoO₄) binary mixtures (2nd and 3rd heating/cooling cycles only)

Mol% of K₂MoO₄	T_{Onset} (°C) 2nd heating	T_{Onset} (°C) 3rd heating	T_{Peak} (°C) 2nd heating	T_{Peak} (°C) 3rd heating	Mass Change (%)
70	389.3	389.3	921.8	921.8	0.24*
80	390.0	390.0	921.0	921.0	0.26*

* There was a small mass gain associated with oxidation due to impurity traces of oxygen in N₂(g).

** These measurements were performed using the SDT Q600 TA Instrument (New Castle, DE, U.S.A.).

7. The (Na₂CrO₄ + Na₂MoO₄) system

Table D6 DSC-TGA results for (Na₂CrO₄ + Na₂MoO₄) binary mixtures (2nd and 3rd heating/cooling cycles only)

Mol% of Na₂MoO₄	T_{Onset} (°C) 2nd heating	T_{Onset} (°C) 3rd heating	T_{Peak} (°C) 2nd heating	T_{Peak} (°C) 3rd heating	Mass Change (%)
10	405.2	405.9	445.7*	445.2*	-0.87
			773.8	774.0	-1.12
50	471.1	468.9	721.1	721.3	-0.56
30	383.1	381.6	740.3	740.5	-0.56
70	531.3	532.2	711.5	711.5	-0.21
90	598.9	599.5	699.3	699.3	0.04**

* These temperature values were taken at the maximum of the peak (and not at the onset of the peak) since these were very low intensity peaks.

** There was a small mass gain associated with oxidation due to impurity traces of oxygen in Ar(g).

8. The (K₂CrO₄ + K₂MoO₄) system

Table D7 DSC-TGA results for (K₂CrO₄ + K₂MoO₄) binary mixtures (2nd and 3rd heating/cooling cycles only)

Mol% of K ₂ MoO ₄	<i>T</i> _{Onset} (°C) 2 nd heating	<i>T</i> _{Onset} (°C) 3 rd heating	<i>T</i> _{Peak} (°C) 2 nd heating	<i>T</i> _{Peak} (°C) 3 rd heating	Mass Change (%)
75	460.7	460.7	936.7	936.7	-0.25
85	452.4	452.4	936.2	936.2	-0.18
95	452.7	452.7	936.3	936.3	-0.10

9. The (Na₂MoO₄ + K₂MoO₄) system

Table D8 DSC-TGA results for mechanical mixtures of pre-treated reagents Na₂MoO₄ and K₂MoO₄ in the (Na₂MoO₄ + K₂MoO₄) binary sub-system (2nd and 3rd heating/cooling cycles only)

Mol% of K ₂ MoO ₄	<i>T</i> _{Onset} (°C) 2 nd heating	<i>T</i> _{Onset} (°C) 3 rd heating	<i>T</i> _{Peak} (°C) 2 nd heating	<i>T</i> _{Peak} (°C) 3 rd heating	Mass Change (%)
5	453.5	453.5	684.1	684.1	-0.13
	520.2	520.7			
	623.5	623.2			
15			288.9*	288.9*	-0.23
			670.4	670.4	
	410.9	411.5			

	659.6	659.6			
30	313.7	314.5	678.1	678.1	0.05**
40	272.0	275.5	689.0	689.0	-0.13
	681.5	681.4			
50	673.0	673.5	708.0	708.0	-0.21
			728.6	728.6	
65	649.0	647.5	746.3	748.7	0.69**
			792.3	792.3	
80	555.7	556.6	807.8	807.8	-0.35
			851.2	849.8	
90			343.6*	343.6*	-0.15
			419.4*	421.9*	
			484.9*	484.6*	
			894.4	894.1	
95	458.6	458.5	913.7	913.7	-0.29

* These temperature values were taken at the maximum of the peak (and not at the onset of the peak) since these were very low intensity peaks.

** There was a small mass gain associated with oxidation due to impurity traces of oxygen in Ar(g).

The binary compositions listed in Table D9 and investigated by DSC-TGA were obtained by adding an excess of Na₂MoO₄ or K₂MoO₄ to a sample of molybdenum-glaserite with the nominal composition of (35 mol% Na₂MoO₄ + 65 mol% K₂MoO₄) equilibrated at 400°C for four weeks.

Table D9 DSC-TGA results for binary mixtures obtained by addition of an excess of Na₂MoO₄ or K₂MoO₄ to an equilibrated sample with the nominal composition (35 mol% Na₂MoO₄ + 65 mol% K₂MoO₄) (1st, 2nd and 3rd heating/cooling cycles, and all temperatures in °C)

Mol% of K₂MoO₄	<i>T</i>_{Onset} 1st heating	<i>T</i>_{Onset} 2nd heating	<i>T</i>_{Onset} 3rd heating	<i>T</i>_{Peak} 1st heating	<i>T</i>_{Peak} 2nd heating	<i>T</i>_{Peak} 3rd heating	Mass Change (%)
62.5	455.8	-	-	743.4	743.9	743.9	0.02*
	650.5	655.1	625.3	783.4	783.7	783.7	
70.0	325.3	-	-	752.7	755.3	754.8	-0.22
	642.6	641.4	642.0	797.5	799.5	799.0	

* There was a small mass gain associated with oxidation due to impurity traces of oxygen in Ar(g).

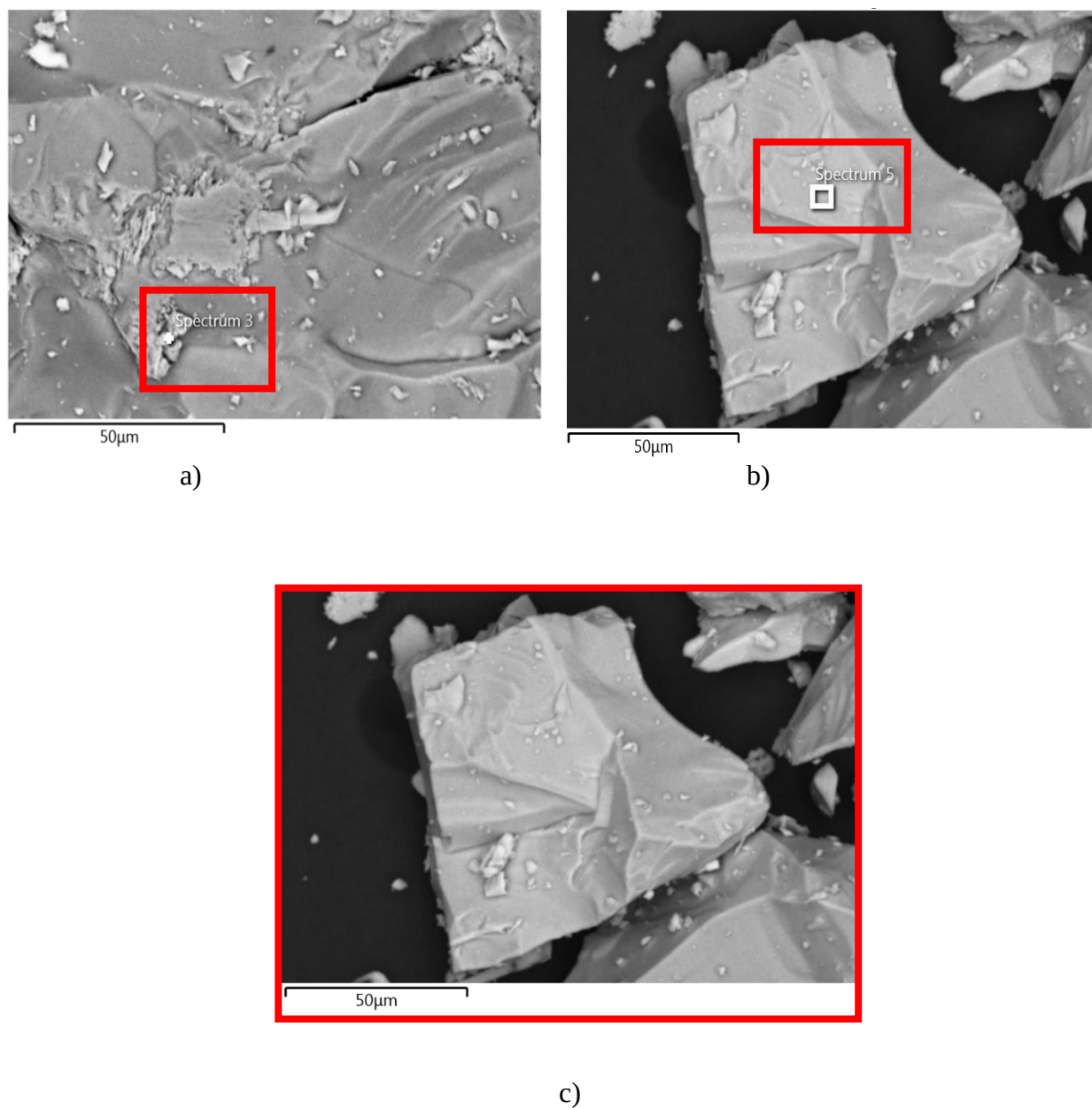


Figure D1 SEM secondary electron images of the equilibrated molybdenum-glaserite sample with the nominal composition of (35 mol% Na_2MoO_4 + 65 mol% K_2MoO_4): a) spectrum 3, b) spectrum 5, and c) spectrum 7

Molybdate-based common-cation ternary sub-systems

2. The ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) system

Calculations are presented below for three of the six isoplethal sections measured by Mateiko and Bukhalova [1] using visual observations.

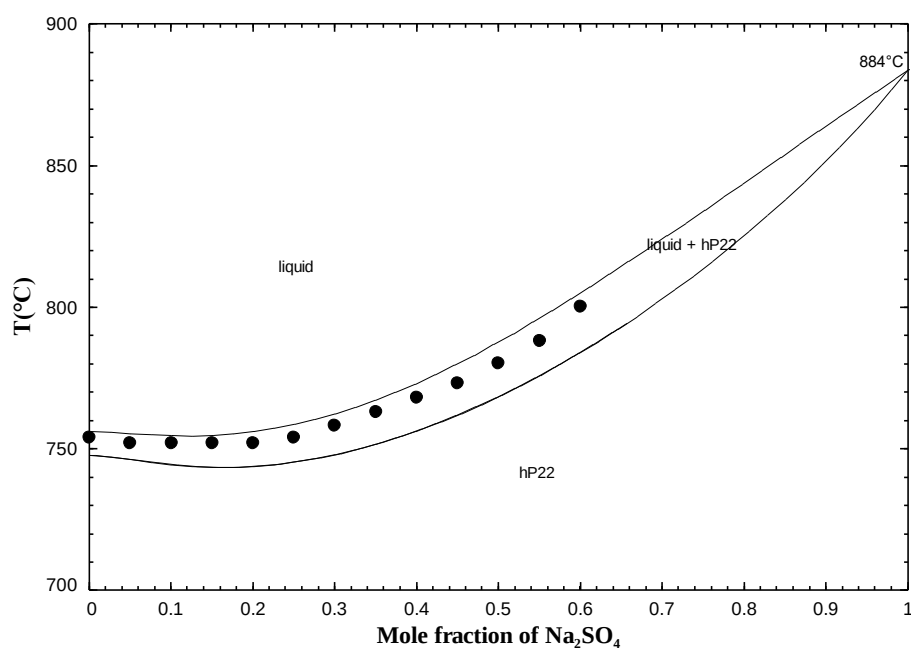


Figure D2 Calculated isoplethal section in the ($\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4$) system ($(\text{Na}_2\text{CrO}_4)_{0.75}(\text{Na}_2\text{MoO}_4)_{0.25}-\text{Na}_2\text{SO}_4$, section II). Experimental data from Mateiko and Bukhalova [1] (●)

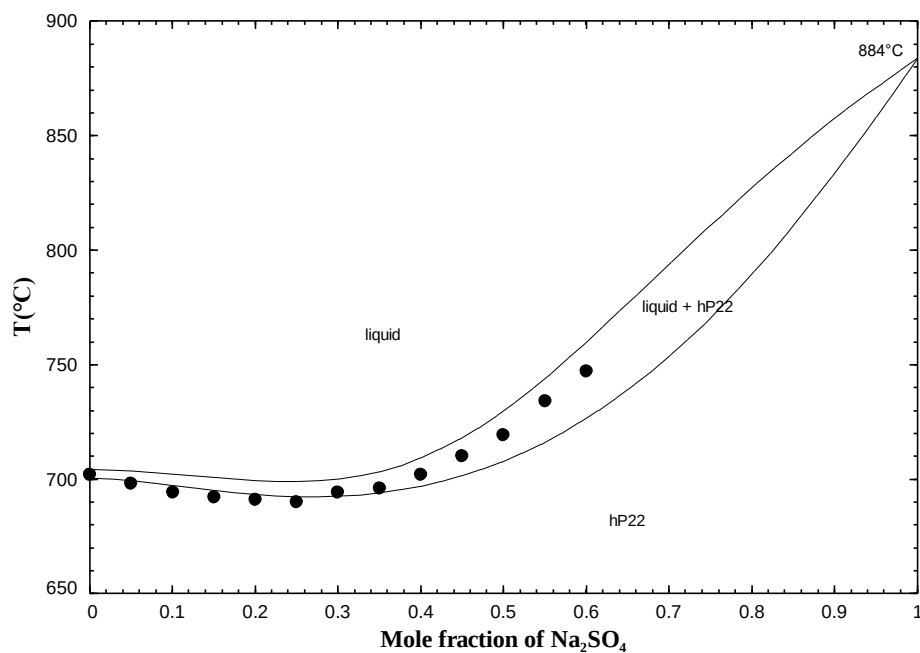


Figure D3 Calculated isoplethal section in the $(\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4)$ system $((\text{Na}_2\text{CrO}_4)_{0.25}(\text{Na}_2\text{MoO}_4)_{0.75} - \text{Na}_2\text{SO}_4)$, section III). Experimental data from Mateiko and Bukhalova [1] (●)

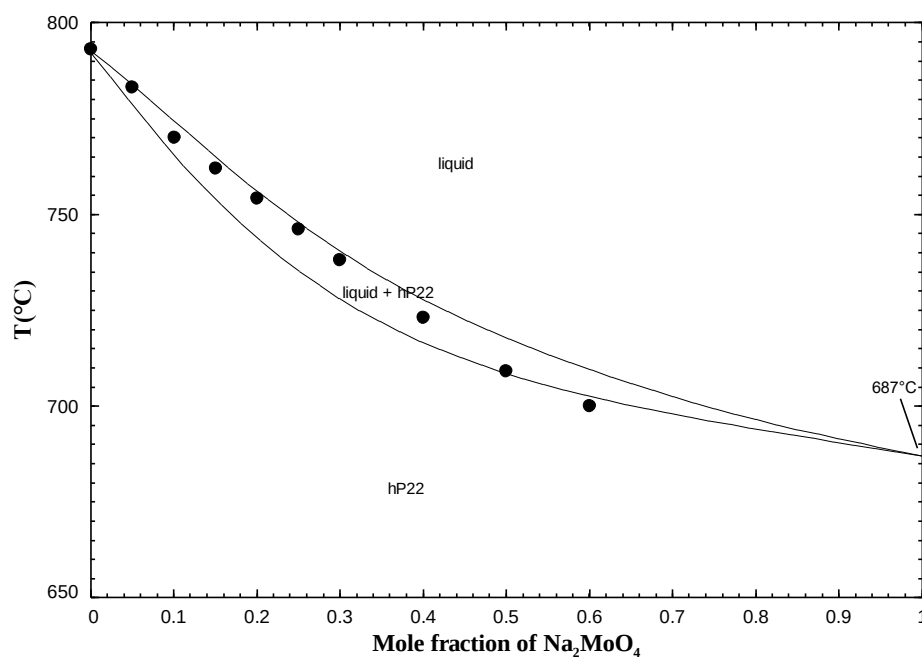


Figure D4 Calculated isoplethal section in the $(\text{Na}_2\text{SO}_4 + \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{MoO}_4)$ system $((\text{Na}_2\text{SO}_4)_{0.25}(\text{Na}_2\text{CrO}_4)_{0.75} - \text{Na}_2\text{MoO}_4)$, section V). Experimental data from Mateiko and Bukhalova [1] (●)

Molybdate-based ternary reciprocal sub-systems

1. The (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system

Calculations are presented below for twelve of the seventeen isoplethal sections measured by Bukhalova and Mateiko [2] using the visual-polythermal method. In these 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.

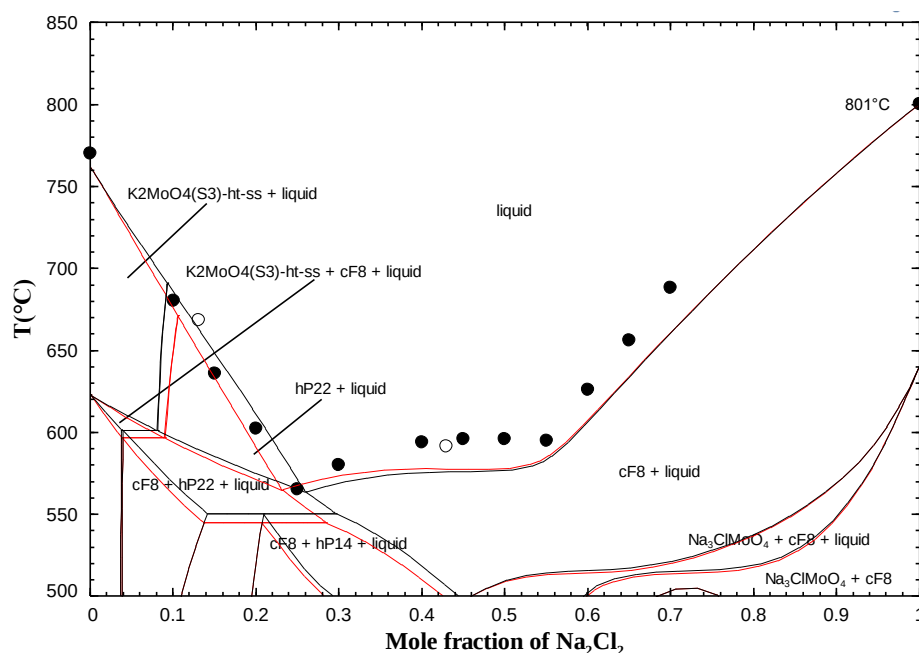


Figure D5 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system ((K₂Cl₂)_{0.25}(K₂MoO₄)_{0.75}-Na₂Cl₂, section II). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

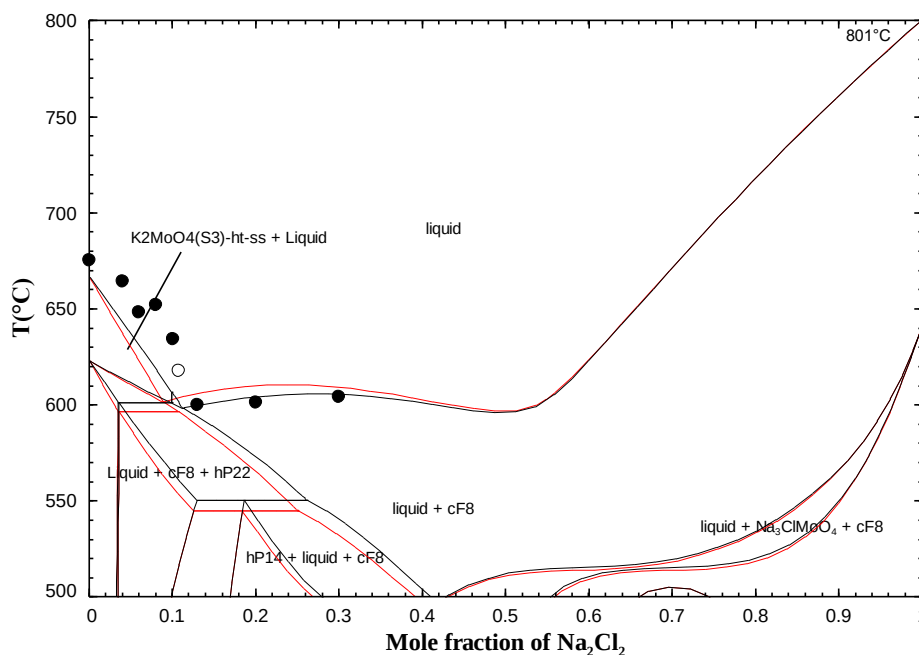


Figure D6 Calculated isoplethal section in the $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4)$ system $((\text{K}_2\text{Cl}_2)_{0.40}(\text{K}_2\text{MoO}_4)_{0.60}\text{-Na}_2\text{Cl}_2$, section III). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

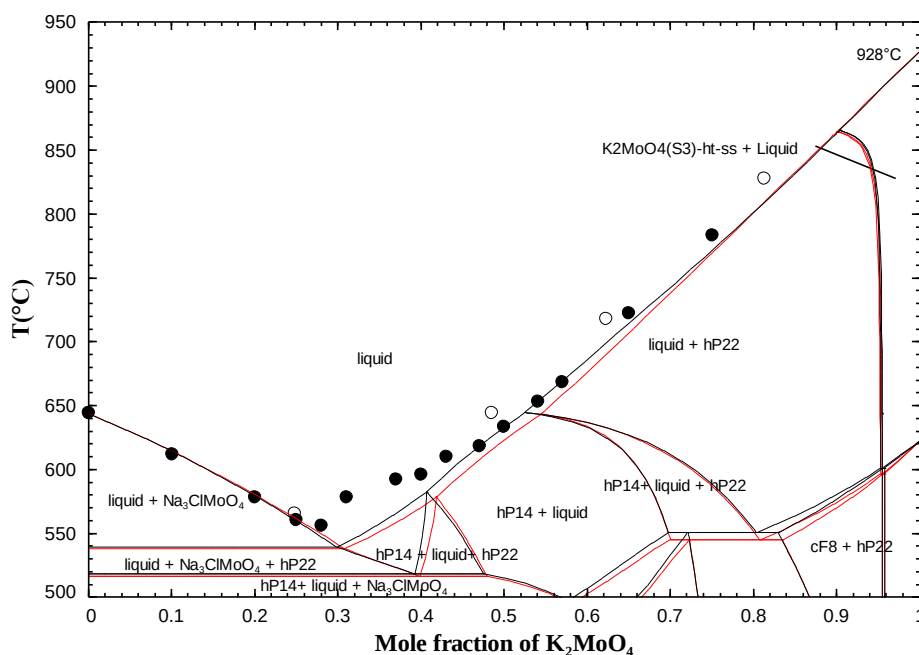


Figure D7 Calculated isoplethal section in the $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4)$ system $((\text{Na}_2\text{MoO}_4)_{0.67}(\text{Na}_2\text{Cl}_2)_{0.33}\text{-K}_2\text{MoO}_4$, section IV). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

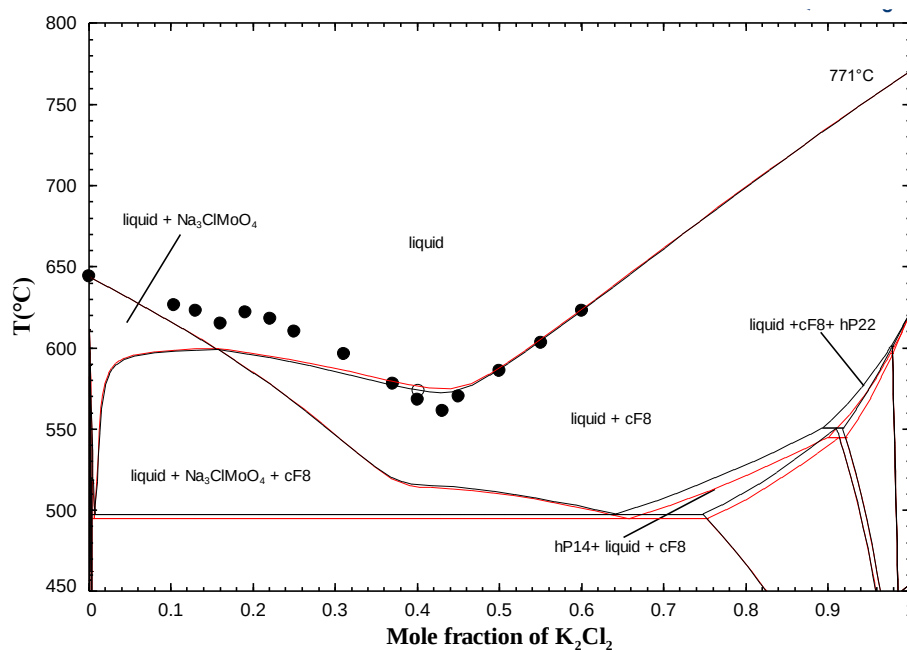


Figure D8 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system ((Na₂MoO₄)_{0.67}(Na₂Cl₂)_{0.33}-K₂Cl₂, section V). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

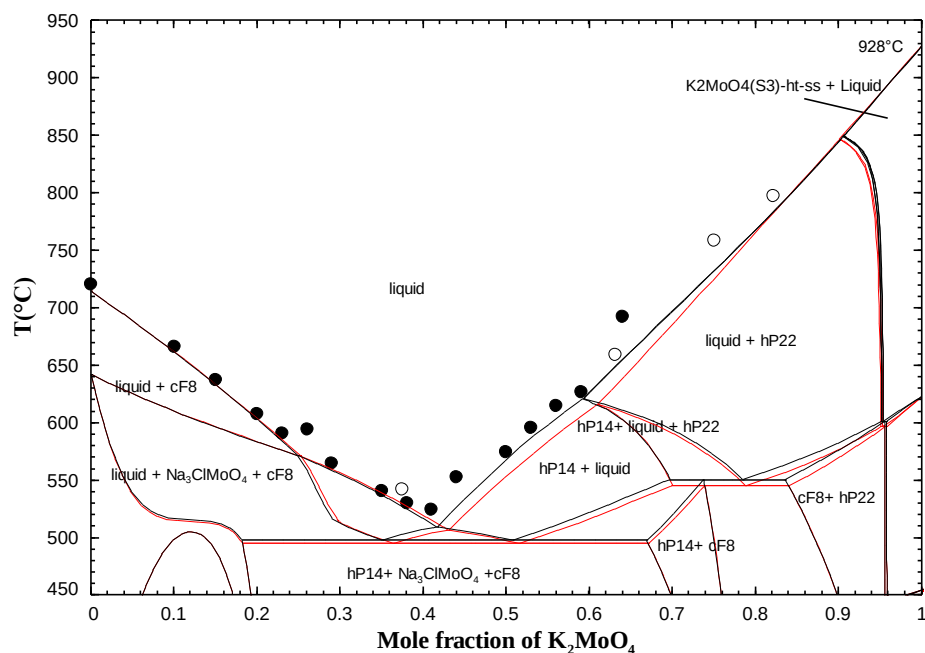


Figure D9 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system ((Na₂MoO₄)_{0.40}(Na₂Cl₂)_{0.60}-K₂MoO₄, section VI). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

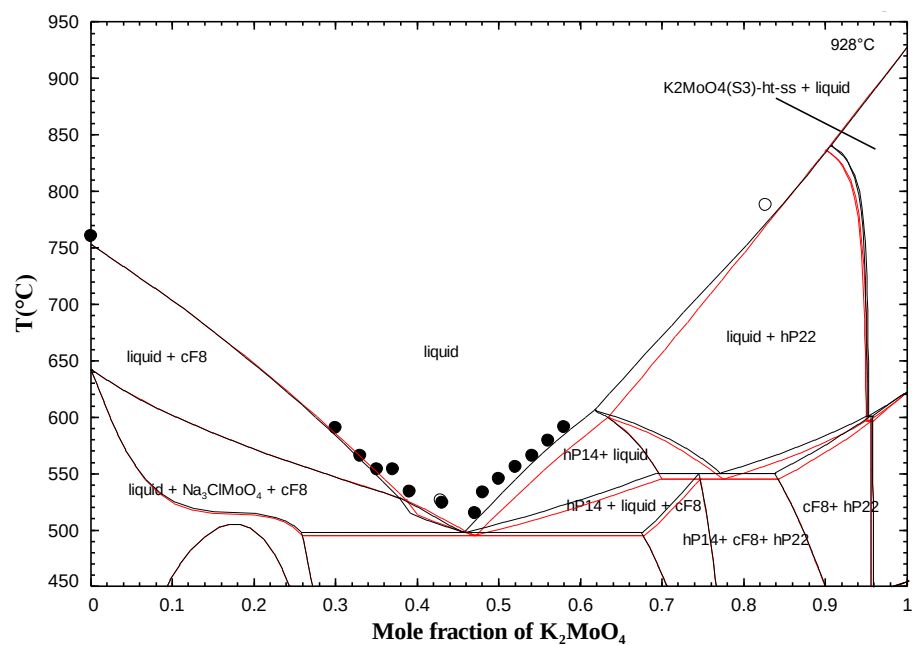


Figure D10 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system

$((\text{Na}_2\text{MoO}_4)_{0.25}(\text{Na}_2\text{Cl}_2)_{0.75}-\text{K}_2\text{MoO}_4$, section VII). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

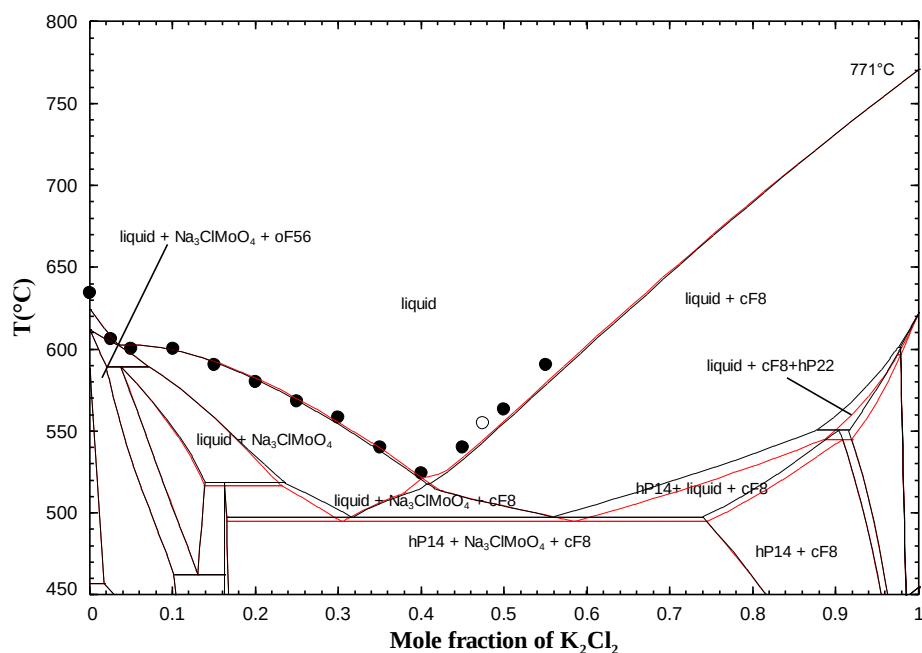


Figure D11 Calculated isoplethal section in the $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4)$ system $((\text{Na}_2\text{MoO}_4)_{0.90}(\text{Na}_2\text{Cl}_2)_{0.10}-\text{K}_2\text{Cl}_2$, section VIII). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2]

(●, ○)

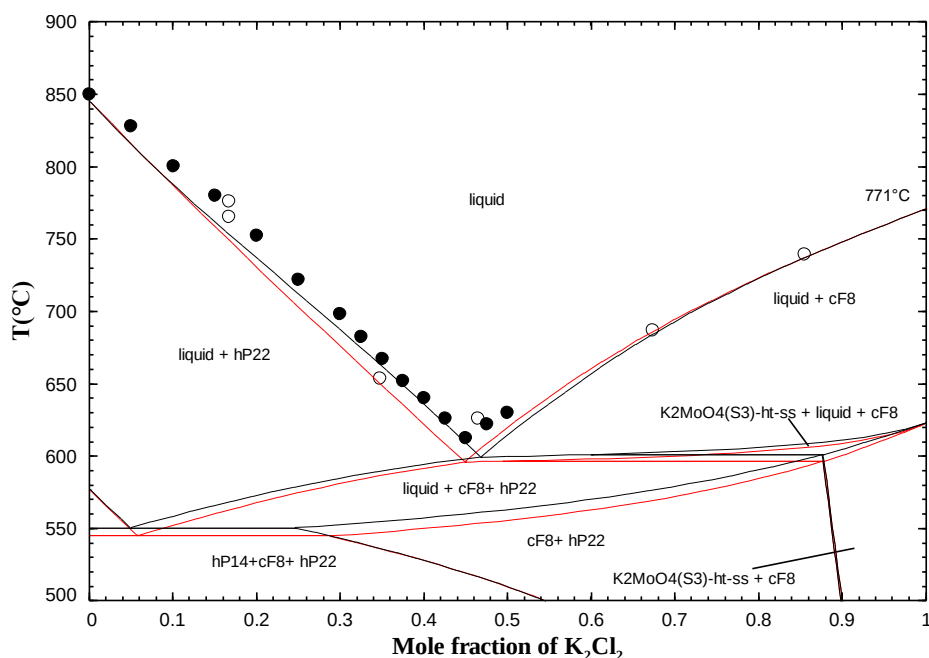


Figure D12 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system ((Na₂MoO₄)_{0.20}(K₂MoO₄)_{0.80}-K₂Cl₂, section X). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

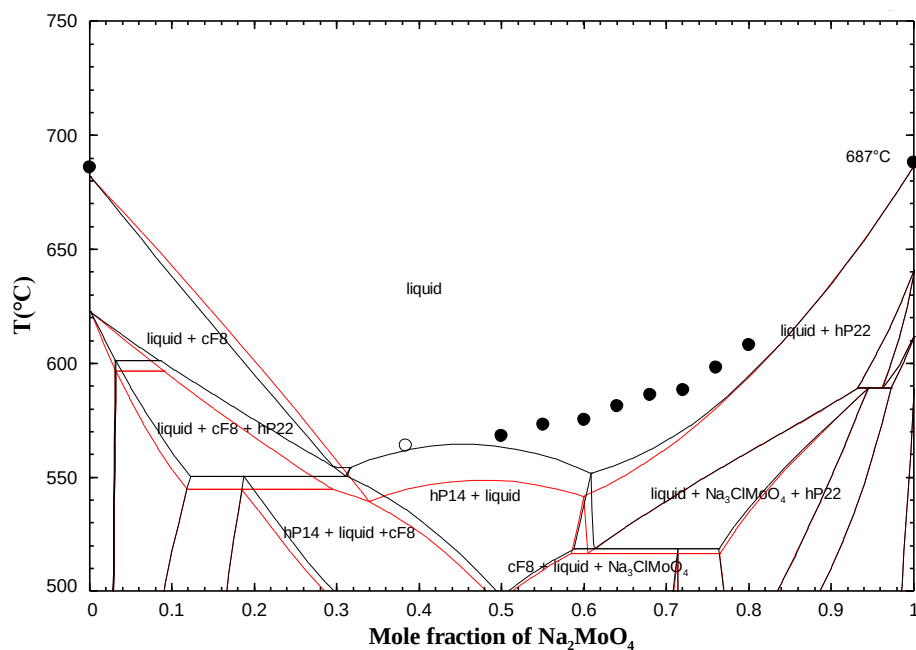


Figure D13 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system ((K₂Cl₂)_{0.62}(K₂MoO₄)_{0.38}-Na₂MoO₄, section XI). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

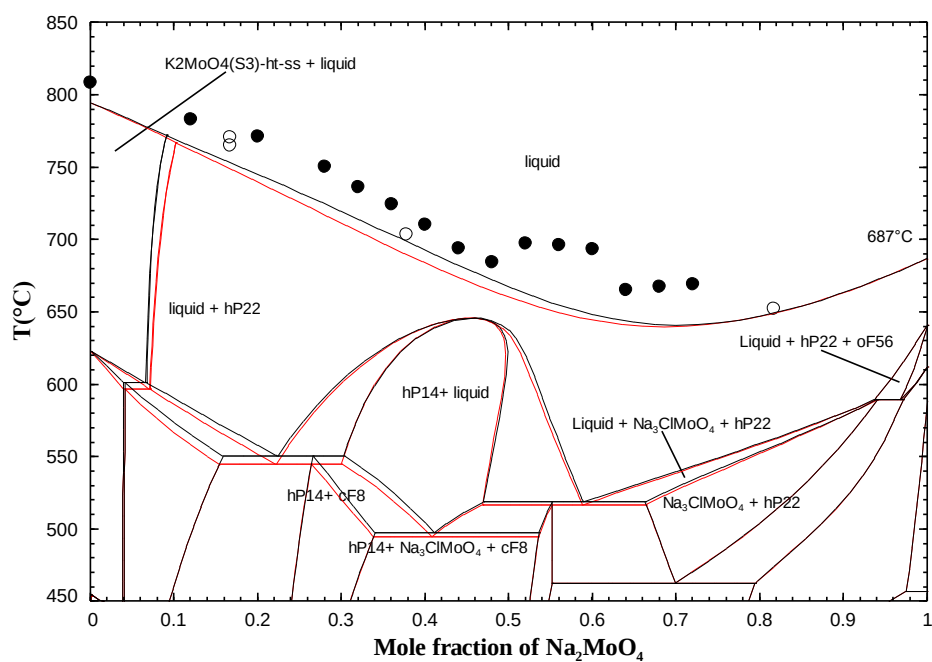


Figure D14 Calculated isoplethal section in the $(\text{NaCl} + \text{KCl} + \text{Na}_2\text{MoO}_4 + \text{K}_2\text{MoO}_4)$ system $((\text{K}_2\text{Cl}_2)_{0.20}(\text{K}_2\text{MoO}_4)_{0.80}\text{-Na}_2\text{MoO}_4$, section XII). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

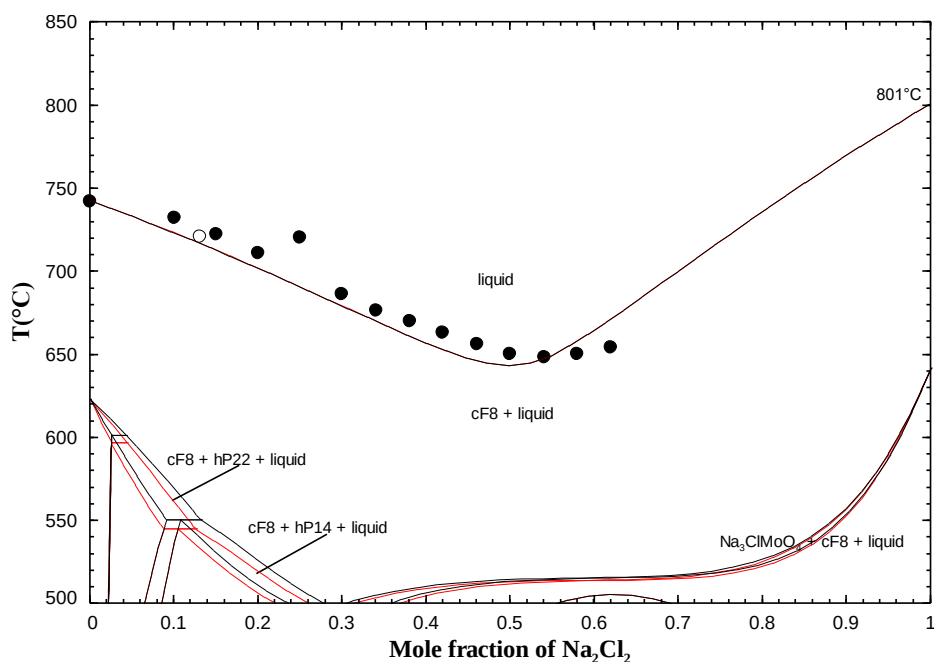


Figure D15 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system ((K₂Cl₂)_{0.85}(K₂MoO₄)_{0.15}-Na₂Cl₂, section XIV). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

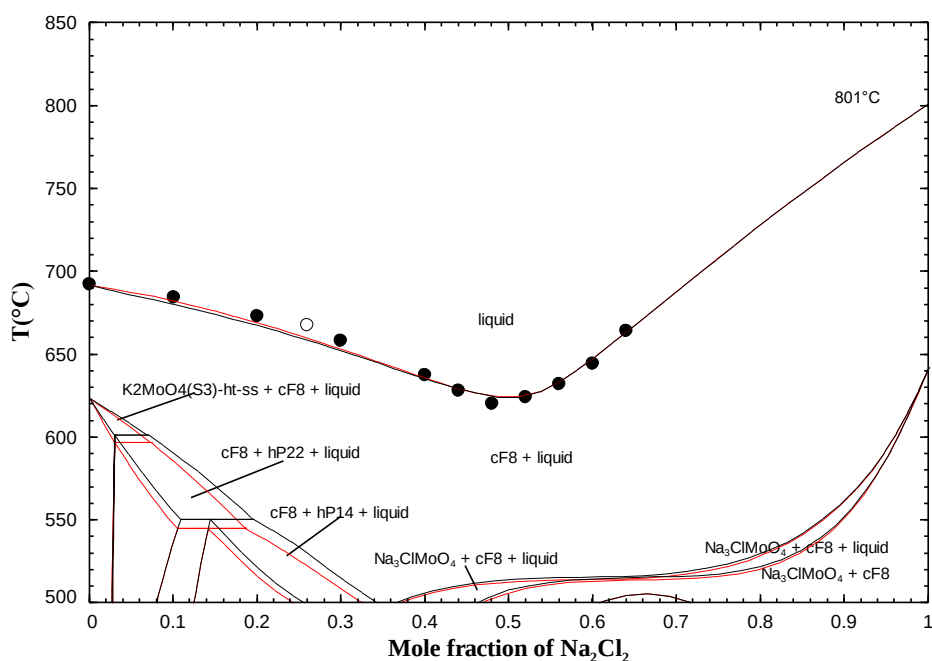


Figure D16 Calculated isoplethal section in the (NaCl + KCl + Na₂MoO₄ + K₂MoO₄) system

$((K_2Cl_2)_{0.65}(K_2MoO_4)_{0.35}-Na_2Cl_2$, section XV). Black lines: final calculations (with one ternary reciprocal parameter); red lines: predictions (without any ternary reciprocal parameter).

Experimental data from Bukhalova and Mateiko [2] (●, ○)

References

- [1] Z. A. Mateiko and G. A. Bukhalova, "Solid solutions in the systems: (1) $Na||SO_4, CrO_4, MoO_4$; (2) $Na||SO_4, CrO_4, WO_4$; (3) $Na||SO_4, MoO_4, WO_4$; (4) $Na||CrO_4, MoO_4, WO_4$," *Zhurnal Neorganicheskoi Khimii*, vol. 4, pp. 2329-34, 1959.
- [2] G. A. Bukhalova and Z. A. Mateiko, "Complex formation and solid solutions in the adiaagonal reciprocal system of the molybdates and chlorides of sodium and potassium," *Zhurnal Obshchei Khimii*, vol. 25, pp. 851-7, 1955.