

Vaporization study of sodium sulphate – potassium sulphate binary system by Knudsen effusion mass spectrometry

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The vaporization of samples of different chemical and phase compositions in the Na₂SO₄–K₂SO₄ system was investigated over the temperature range 1100 K–1400 K by the use of Knudsen effusion mass spectrometry. The gaseous species Na(g), Na₂SO₄(g), K(g), K₂SO₄(g), SO₂(g), O₂(g) and NaKSO₄(g) were identified in the vapour over the samples investigated. The thermodynamic activities of sulphates in the examined system at 1350 K were obtained, which allowed calculating the chemical composition of the vapours present in the high temperature zone of cement kilns.

Keywords: *sulphates vaporization, high temperature mass spectrometry, thermodynamic activities, clinker burning*

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1. Introduction

Raw materials and fuels used in clinker cement industry contain significant amounts of sulphates, chlorides, alkali and alkali earth compounds as well as heavy metal compounds. Some of the substances can react upon burning conditions in clinker kilns releasing volatile species, which evaporate and subsequently condense in the colder parts of the reactor. Simultaneously, raw material flow, continuously introduced into the process, causes secondary steering of the volatile species bounded in the condensed phase towards the high temperature kiln area. In this way, the evaporation and condensation cycle of volatile species produced under specific burning regimes may lead to undesirable gas emission and production breaks necessary for reactor cleaning from substances deposited at its walls.

In order to explain these complex processes, investigations of vaporization thermochemistry of

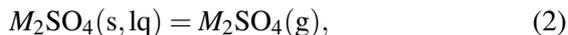
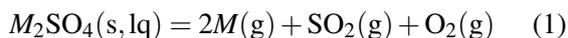
compounds volatile at the clinker burning conditions (sodium, potassium and calcium sulphates and chlorides) are of great importance.

The most typical source of sulphur in clinkers are arcanite (K₂SO₄), apthitalite (solid solution of Na₂SO₄ in K₂SO₄), calcium langbeinite (2CaSO₄·K₂SO₄) and some sulphates substituted in silicates [1]. The total pressure of decomposition products of various sulphates occurring in the cement kiln (calcium sulphate, calcium silicosulphate, calcium aluminosulphate as well as potassium and sodium sulphates) were determined by Choi and Glasser [2] by the use of Knudsen mass loss technique. They emphasized that the evaporation/condensation reactions with sulphur in the kilns are enhanced by the presence of alkali, mostly K and Na. The obtained pressures, much higher than 10 Pa, exceeded the Knudsen-Hertz equation conditions, so the evaluation of calculated values was difficult.

The vaporization of pure sodium or potassium sulphates was described in [3–14]. Two main va-

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porization reactions of alkali sulphates were observed: volatilization accompanied by dissociation process (Eq. 1) and by simple vaporization reaction (Eq. 2):



where $M = K, Na$. There are significant differences between the earliest works concerning the chemical composition of vapour, the values of partial pressures and enthalpies of the vaporization reactions. It is possible, that some experimental problems as reactive Knudsen cell material, wrong temperature calibration or apparatus geometry influenced the results, what was also discussed in details by Halle and Stern [6]. Most of the investigations were carried out by transpiration or Knudsen weight loss techniques without a qualitative analysis of gaseous phase. In these cases the partial pressures of gaseous molecules were recalculated on the basis of the data from thermodynamical bases. Only few of the investigations, including the present vaporization studies, were carried out by mass spectrometry, where the composition of gaseous phase over sulphates was experimentally confirmed [3, 6, 8, 10, 13, 14]. The experimental studies showed that the thermal decomposition reaction was predominant for Na_2SO_4 vaporization what contrasts to the results for K_2SO_4 , where the simple sublimation is preferred. It is also in agreement with the dependence of the vaporization processes (sublimation or dissociation reaction) on the electronegativity ratio of salt forming oxides observed by Lopatin [15].

The thermodynamic functions of pure sulphates are known [15, 17], since they could be calculated on the basis of reliable data on their structure and infrared spectra. Less is known about the vaporization in systems composed of two components, as in the case of Na_2SO_4 and K_2SO_4 . The both sulphates show crystal structure affinity, what is manifested at higher temperatures, where the solid solution of the compounds forms in a full composition range. In such a case the presence of new, complex gaseous species could be also assumed.

The aim of the work was to study the vaporization process of mixed sodium – potassium sulphates, which are mostly responsible for sulphate cycles in cement production technology. The presented investigations were undertaken due to the serious problems mentioned above, occurring in cement kilns. The experiments were carried out by the Knudsen effusion mass spectrometry technique (KEMS), also called high temperature mass spectrometry. In this work, mass spectra of gaseous species observed over the binary system Na_2SO_4 – K_2SO_4 and the thermodynamic characteristics of vaporization processes in the investigated system are presented. The obtained experimental data were used to calculate the chemical composition of the gaseous phase formed under high temperature conditions, typical for clinker burning.

This study was the continuation of the PhD study realized in Institute of Non Metallic Materials, Clausthal University of Technology, Germany [18].

2. Experimental

Eight samples of different chemical compositions were prepared for vaporization studies. Pure potassium sulphate (Riedel-de Haen, anhydrous for analysis > 99 %) and sodium sulphate (Fluka, for analysis 99 %) were used for synthesis in molar ratios as detailed in Table 1. The sulphates were heated to remove moisture in Pt crucibles for 3 hours at 573 K before weighing, then mixed in agate mortar, pressed into pellets and sintered for 6.5 hours at 873 K. The melting temperatures of binary samples were determined by TG/DTA measurements (STA 409 Pc Luxx, Netzsch, 10 Kmin^{-1}). The phase composition of the samples synthesized at 873 K was checked by XRD method (Siemens D5000, $CuK\alpha$ radiation). The phase composition as well as the melting temperatures of the samples agreed well with the phase diagram published by Eysel [19] confirming the formation of a solid solution in the investigated binary system.

The mass spectrometric investigations were carried out with a single-focusing CH5 mass

Table 1. The initial chemical composition of prepared samples and details of the vaporization experiments in the Na₂SO₄–K₂SO₄ system

Sample	$N(\text{Na}_2\text{SO}_4)$ [mole %]	Number of measurement points, n	Temperature range of measurements, ΔT [K]
Na ₂ SO ₄	100	71	1173–1375
Na _{1.7} K _{0.3} SO ₄	85	55	1173–1375
Na _{1.5} K _{0.5} SO ₄	75	65	1171–1385
Na _{1.2} K _{0.8} SO ₄	60	62	1215–1368
Na _{0.9} K _{1.1} SO ₄	45	67	1188–1381
Na _{0.6} K _{1.4} SO ₄	30	64	1212–1375
Na _{0.2} K _{1.8} SO ₄	10	49	1191–1385
K ₂ SO ₄	0	74	1189–1374

spectrometer (Finigann MAT, Bremen, Germany) equipped with a Knudsen cell. The Knudsen cell made of platinum with 0.3 mm diameter effusion orifice was used for the experiments. The temperature was measured with a Pt10Rh thermocouple and a pyrometer (ISQ 5, Impac Infratherm GmbH, Germany), calibrated *in situ* at the melting point of silver. The gaseous species were ionized with electrons energy 70 eV. Between the effusion cell and the ion source region a movable shutter was placed, that enabled us to distinguish between the species vaporizing from the cell and those occurring as residual gases in the apparatus. A secondary electron multiplier was used for ion detection. At the beginning of each vaporization experiment, the samples were heated at constant temperature to achieve stable ionic intensity values. As soon as the thermodynamic equilibrium in the Knudsen cell was achieved, usually in 40–60 minutes, ion intensities were measured at different increasing temperatures. The stability of ion intensities was checked by repeating the measurement at decreased and increased temperatures. The samples were heated up and cooled down, stepwise by 20 K. The details of the vaporization experiments are presented in Table 1.

3. Results

3.1. Partial pressures of vapour species

Identification of the registered ions was carried out from their masses and from the interrup-

tion of the molecular beam with a shutter. When pure Na₂SO₄(s) or K₂SO₄(s) were heated in the Knudsen cell, the following ions were detected: M^+ , M_2O^+ , $M_2SO_4^+$, SO^+ , SO_2^+ , O_2^+ ($M = \text{Na}$ or K). Additionally, in the mass spectra of mixed Na_{2-x}K_xSO₄ samples, NaKO⁺ and NaKSO₄⁺ ions were registered. Both ions were assumed to originate from NaKSO₄(g). The species was for the first time detected and identified in the present study. Assignments of other ions to their neutral precursors were made on the basis of available data (APs) and the rule that ions originating in the same species show the same temperature dependency. The appearance potentials of ions observed in the mass spectra during vaporization studies of Na₂SO₄ and K₂SO₄ were determined in [3, 6, 8, 13, 14]. Simple ionization and fragmentation processes were assumed for appearance of SO₂⁺ and SO⁺ from SO₂(g) [3, 6, 8, 13, 14]. The ions K⁺ (AP = 4.4 ± 0.5 eV [3] or 4.5 ± 0.3 eV [13]) and Na⁺ (AP = 5.0 ± 0.5 eV [3] or 5.0 ± 0.3 eV [14]) were assumed to derive from K(g), Na(g) species, respectively. This finding was previously confirmed by other authors [6, 8]. During vaporization study of pure potassium sulphate Ficalora et al. [3] and Lau and co-workers [13, 14] observed also M₂O⁺ and M₂SO₄⁺ ions. They concluded that both of them originated from M₂SO₄(g), what was in agreement with the observations in [6]. Surprisingly Na₂O⁺ and Na₂SO₄⁺ were not observed in [3], what is in contradiction with other results [8, 14]. The AP value for Na₂O⁺ (9.9 ± 1.0 eV) determined in [8] is significantly lower than that obtained by Lau et

Table 2. The assignments of ions to their neutral precursors observed upon vaporizing the Na_2SO_4 – K_2SO_4 samples.

Gaseous species	Ions detected
O_2 (g)	O_2^+
SO_2 (g)	SO^+
Na (g)	Na^+
Na_2SO_4 (g)	Na_2O^+
K (g)	K^+
K_2SO_4 (g)	K_2O^+
NaKSO_4 (g)	NaKO^+
	NaKSO_4^+

al. (11.5 ± 0.5 eV [14]) but the both works confirm that the ion must be an ionization fragment of Na_2SO_4 (g). In contrast to these findings are the results of Kosugi [10] who assumed that K^+ and K_2O^+ are ionization products of K_2O (g). He assumed that the same slope value of $\ln(I^+T)$ vs. $1/T$ plot for both ions indicates that the K^+ must be a fragment of K_2O , but no attempt to estimate the AP's for the ions was made.

In this study both ion ratios $\text{Na}_2\text{O}^+/\text{Na}_2\text{SO}_4^+$ and $\text{K}_2\text{O}^+/\text{K}_2\text{SO}_4^+$ at all temperatures were constant what was an additional proof for the partial fragmentation of $M_2\text{SO}_4$ (g) species to the $M_2\text{O}^+$ ions. The assignments of all registered ions to their neutral precursors are presented in Table 2. The fragmentation coefficients of the molecules Na_2SO_4 (g) and K_2SO_4 (g) to $M_2\text{O}^+$ ions were calculated as an average ratio of measured ions intensities during vaporization studies of pure sulphates. The values of 1.30 ± 0.12 and 1.13 ± 0.14 for $I(\text{Na}_2\text{O}^+)/I(\text{Na}_2\text{SO}_4^+)$ and $I(\text{K}_2\text{O}^+)/I(\text{K}_2\text{SO}_4^+)$ were obtained respectively.

The temperature dependencies of observed ion currents during vaporization of Na_2SO_4 or K_2SO_4 are presented in the Figs. 1–2.

The partial pressures $p(i)$ of the species i at the temperature T were obtained from the equation:

$$p(i) = \frac{kT \sum I(i)}{\sigma(i)}, \quad (3)$$

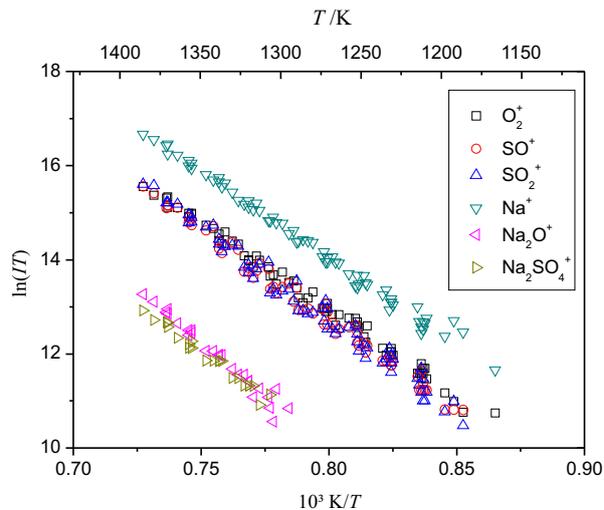


Fig. 1. The temperature dependence of ion currents during vaporization of Na_2SO_4 .

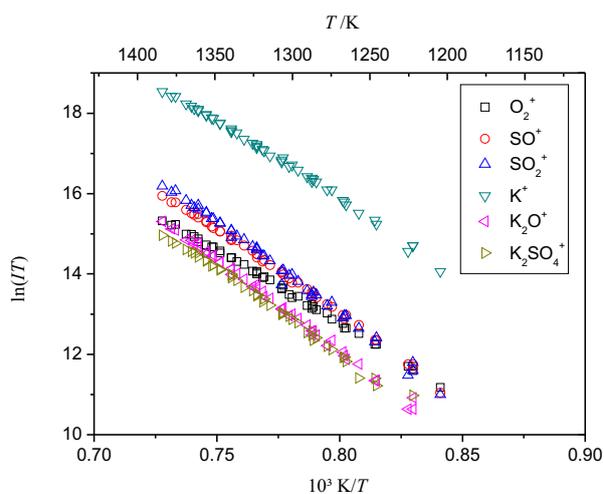


Fig. 2. The temperature dependence of ion currents during vaporization of K_2SO_4 .

where k is an apparatus calibration factor and $\sigma(i)$ is the ionization cross section of species i . The $\sum I(i)$ is the sum of all ion intensities originating in ionization and/or fragmentation of species i . In the presented study the apparatus constant was determined by vaporization of pure silver at its melting point. The values of the relative ionization cross sections $\sigma(i)$ given in parentheses were used for the following gaseous species i : Ag (5.35), O_2 (1.25), K (5.90), Na (4.10), SO_2 (6.93), K_2SO_4 (16.10), Na_2SO_4 (13.36) and KNaSO_4 (14.73). They were

estimated on the basis of the cross sections of atoms given in [21–24] and for the compounds from the Eq. 4 proposed by Drowart et al. [21].

$$\sigma(A_mB_n) = 0.75[n\sigma(A) + m\sigma(B)]. \quad (4)$$

The determined partial pressures of gaseous species over the system investigated were evaluated by the Eq. 3 for each measurement temperature. In our work, because of high electron energy of 70 eV, the fragmentation paths other than assumed are possible, for example origin of M^+ as in M_2SO_4 or $NaKSO_4$. They were neglected in the present study, therefore the obtained partial pressures should be considered only as approximate values. Table 3 presents the obtained partial pressures of different species at 1350 K.

3.2. Thermodynamic activities of sulphates in the Na_2SO_4 – K_2SO_4 system

The thermodynamic activity of each component was evaluated at 1350 K using two different methods: by comparison of ion current values of $Na_2SO_4^+$ and $K_2SO_4^+$ over binary samples and over pure substances (ion to ion method) and by ion intensity ratio integration method.

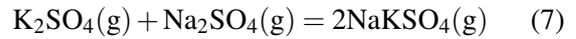
The direct comparison of the ion intensities is possible only when the calibration constant in the measurements is the same (the same measurement conditions, the same Knudsen cell). The following

equations were used for determination of sulphate activities in the $Na_{2-x}K_xSO_4$ samples:

$$a(Na_2SO_4) = I(Na_2SO_4^+)/I(Na_2SO_4^+)^{Ref.} \quad (5)$$

$$a(K_2SO_4) = I(K_2SO_4^+)/I(K_2SO_4^+)^{Ref.} \quad (6)$$

where $I(M_2SO_4^+)^{Ref.}$ denotes the average ion current at 1350 K upon vaporizing the reference sample (pure K_2SO_4 or Na_2SO_4). For the samples where no signal of $M_2SO_4^+$ could be registered, the value was calculated from the equilibrium constant:



$$\begin{aligned} K_p/A &= \frac{p(NaKSO_4)^2}{p(Na_2SO_4) \cdot p(K_2SO_4)A} \\ &= \frac{I(NaKSO_4^+)^2}{I(K_2SO_4^+) \cdot I(Na_2SO_4^+)} \\ &= 0.838 \pm 0.149, \end{aligned} \quad (8)$$

where A is a constant value.

The obtained activities of sulphates are shown in Table 5.

The activities of the compounds were also evaluated by ion intensity ratio integration method developed by Lyubimov et al. [24], Belton and Fruehan [25], as well as Neckel and Wagner [26, 27]. In the binary system the activity coefficient γ of sulphate can be calculated using Gibbs-Duhem relation (Eq. 9 and 10):

$$\ln \gamma_{Na_2SO_4} = - \int_1^{N_{Na_2SO_4}} N_{K_2SO_4} d \left[\ln \left(\frac{I_{K_2SO_4^+} \cdot N_{Na_2SO_4}}{I_{Na_2SO_4^+} \cdot N_{K_2SO_4}} \right) \right] \quad (9)$$

$$\ln \gamma_{K_2SO_4} = - \int_1^{N_{K_2SO_4}} N_{Na_2SO_4} d \left[\ln \left(\frac{I_{Na_2SO_4^+} \cdot N_{K_2SO_4}}{I_{K_2SO_4^+} \cdot N_{Na_2SO_4}} \right) \right], \quad (10)$$

where γ_i is the activity coefficient of sulphate, defined as $\gamma_i = \frac{a_i}{N_i}$ and N_i is the molar fraction of component i .

Table 3. The partial pressure values of volatile species over $\text{Na}_{2-x}\text{K}_x\text{SO}_4$ samples at 1350 K.

Sample	p/Pa						
	O_2	SO_2	Na	Na_2SO_4	K	K_2SO_4	NaKSO_4
Na_2SO_4	0.31	0.46	1.2	$1.9 \cdot 10^{-3}$	–	–	–
$\text{Na}_{1.7}\text{K}_{0.3}\text{SO}_4$	0.48	0.18	2.6	$1.4 \cdot 10^{-3}$	0.77	–	$1.1 \cdot 10^{-3}$
$\text{Na}_{1.5}\text{K}_{0.5}\text{SO}_4$	0.64	0.23	1.9	$1.0 \cdot 10^{-3}$	1.0	$6.8 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$
$\text{Na}_{1.2}\text{K}_{0.8}\text{SO}_4$	0.84	0.47	1.3	$7.4 \cdot 10^{-3}$	1.7	$1.7 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$
$\text{Na}_{0.9}\text{K}_{1.1}\text{SO}_4$	0.92	0.77	1.3	$4.5 \cdot 10^{-3}$	2.5	$3.5 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
$\text{Na}_{0.6}\text{K}_{1.4}\text{SO}_4$	1.2	0.45	0.69	–	3.0	$4.8 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
$\text{Na}_{0.2}\text{K}_{1.8}\text{SO}_4$	1.2	1.0	0.30	–	5.4	0.10	$9.7 \cdot 10^{-3}$
K_2SO_4	0.94	0.80	–	–	5.7	0.12	–

Table 4. The intensities of K_2SO_4^+ , Na_2SO_4^+ and NaKSO_4^+ at 1350 K

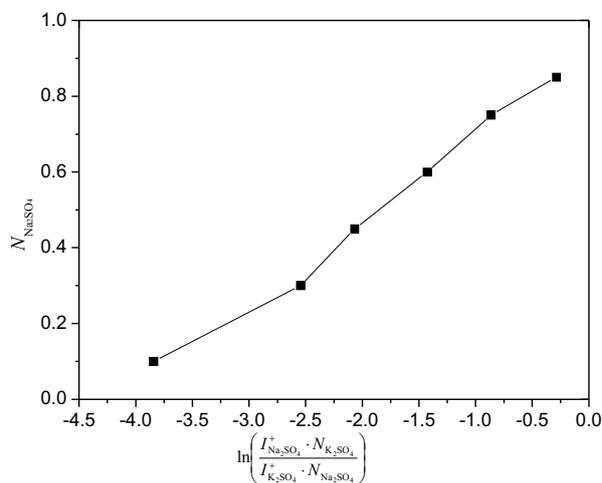
Sample	Na_2SO_4^+	K_2SO_4^+	NaKSO_4^+
Na_2SO_4	181	–	–
$\text{Na}_{1.7}\text{K}_{0.3}\text{SO}_4$	130	(33.0) ^a	60.4
$\text{Na}_{1.5}\text{K}_{0.5}\text{SO}_4$	99.8	82.4	76.9
$\text{Na}_{1.2}\text{K}_{0.8}\text{SO}_4$	71.3	199	115
$\text{Na}_{0.9}\text{K}_{1.1}\text{SO}_4$	43.6	417.3	126
$\text{Na}_{0.6}\text{K}_{1.4}\text{SO}_4$	(19.3) ^a	577.1	96.3
$\text{Na}_{0.2}\text{K}_{1.8}\text{SO}_4$	(2.87) ^a	1210	53.7
K_2SO_4	–	1473	–

^acalculated from Eq. 8.

The graph shown in Fig. 3 was used for the integration yielding the activity coefficient of K_2SO_4 . The computations were carried out using mean ion intensities at 1350 K presented in Table 4. Table 5 shows the chemical activities of sulphates at 1350 K obtained by this method.

4. Discussion

The Na_2SO_4 – K_2SO_4 system is known to build a continuous solid solution at temperatures exceeding 856 K [19]. The change in the chemical activity of pure compounds in systems where the solubility of components is observed is usually accompanied by the negative deviations from the Raoult's law. During our study the vapour pressures of sodium and potassium sulphates showed such kind of behaviour (Fig. 4). The change in the chemical acti-

Fig. 3. The integration plot for the thermodynamic activity of K_2SO_4 calculation (1350 K).

values of the both investigated sulphates in the two component system is also shown in the Fig. 5.

In the vapour over $\text{Na}_{2-x}\text{K}_x\text{SO}_4$ samples a new gaseous species (NaKSO_4) was identified. Since the maximal partial pressures of $M_2\text{SO}_4(\text{g})$ over complex systems are limited by the chemical activity of respective sulphate, the formation of the NaKSO_4 molecule could be responsible for the additional gaseous mass transport in the binary system. The volatilization of sulphates in form of $\text{NaKSO}_4(\text{g})$ is independent of the O_2 and SO_2 partial pressures and could be a significant factor enhancing the mass transport during sulphates cycle in cement kilns.

Table 5. The thermodynamic activities of sulphates in the binary system $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4$ obtained by the ion to ion method and by ion intensity ratio integration computation.

Sample	$a(\text{Na}_2\text{SO}_4)$			$a(\text{K}_2\text{SO}_4)$		
	Eq. 5	Eq. 9	Mean value	Eq. 6	Eq. 10	Mean value
$\text{Na}_{1.7}\text{K}_{0.3}\text{SO}_4$	0.718	0.792	0.755 ± 0.052	0.022	0.028	0.025 ± 0.004
$\text{Na}_{1.5}\text{K}_{0.5}\text{SO}_4$	0.551	0.629	0.590 ± 0.054	0.056	0.074	0.065 ± 0.013
$\text{Na}_{1.2}\text{K}_{0.8}\text{SO}_4$	0.394	0.420	0.407 ± 0.018	0.135	0.172	0.154 ± 0.026
$\text{Na}_{0.9}\text{K}_{1.1}\text{SO}_4$	0.241	0.230	0.236 ± 0.008	0.283	0.332	0.308 ± 0.035
$\text{Na}_{0.6}\text{K}_{1.4}\text{SO}_4$	0.107	0.114	0.110 ± 0.005	0.392	0.505	0.449 ± 0.080
$\text{Na}_{0.2}\text{K}_{1.8}\text{SO}_4$	0.016	0.014	0.015 ± 0.002	0.821	0.858	0.840 ± 0.026

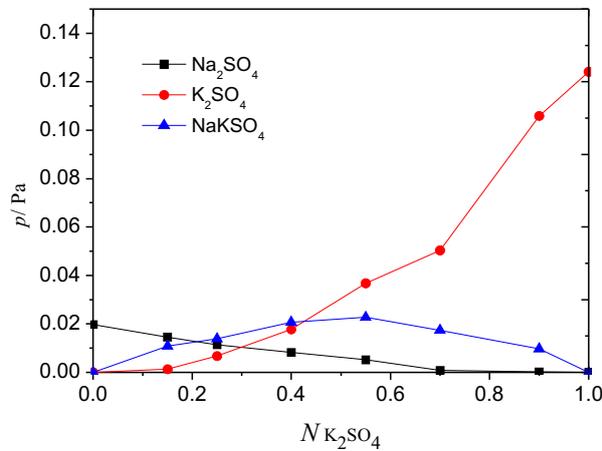
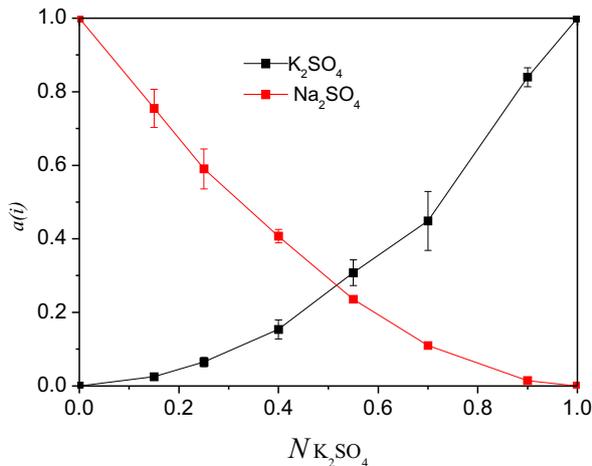

 Fig. 4. The average partial pressures of K_2SO_4 , Na_2SO_4 and NaKSO_4 at 1350 K for samples with different molar fraction of K_2SO_4 .

 Fig. 5. The dependence of the thermodynamic activities of the respective sulphates in the $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4$ system at 1350 K on the molar fraction of K_2SO_4 .

Table 6. composition of coal assumed for calculations [27].

Element	Dry fuel composition [mass %]
C	88.4
H	4.9
S	1.2
N	1.3
O	4.2

Since the presence of the NaKSO_4 species could influence the chemical composition of the gaseous phase in the cement kiln, following calculations were made to estimate the partial pressures of molecules containing sodium and potassium in the vapour under technological regimes of cement production. The partial pressures of Na_2SO_4 , K_2SO_4 , K and Na were calculated for a hot zone of cement kiln based on the equilibrium constant values of reactions (Eq. 1) and (Eq. 2) [17].

The values of the partial pressures of $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$, which are 90 Pa and 2000 Pa, respectively, were estimated on the basis of assumed fuel composition medium value typical for clinker production [28] (Table 6). The combustion process was assumed to be the dominant source of SO_2 and O_2 production.

The partial pressures of $\text{NaKSO}_4(\text{g})$ were obtained using the equilibrium constant (Eq. 8) of reaction (Eq. 7). The activities of both sulphates were adopted as obtained in the present study (Table 5). The values of $p(i)$ for $M(\text{g})$, $\text{O}_2(\text{g})$, $\text{SO}_2(\text{g})$, $M_2\text{SO}_4(\text{g})$ and $\text{NaKSO}_4(\text{g})$, calculated for the high temperature zone at 1723 K for different molar fractions of K_2SO_4 , are summarized in Fig. 6.

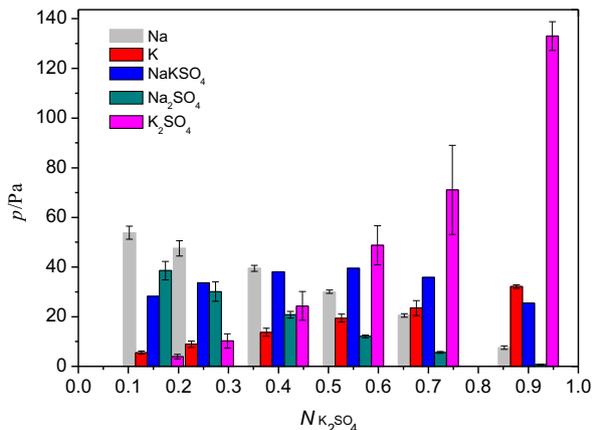


Fig. 6. The partial pressures of alkali sulphates in the hot zone of cement kiln calculated for a temperature of 1723 K, where $p(\text{SO}_2) = 90$ Pa and $p(\text{O}_2) = 200$ Pa.

5. Conclusions

The thermochemical properties of the binary $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4$ system were investigated by the Knudsen effusion mass spectrometry. The new species $\text{NaKSO}_4(\text{g})$ in the gaseous phase was detected for the first time. The thermodynamic activities of sulphates at 1350 K for the $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4$ binary system were obtained, which indicate negative deviations from Raoult's rule. The gaseous composition in the hot zone of cement kiln was estimated using thermodynamical functions obtained in the present study. The most volatile species of alkali sulphates in the hot zone of cement kiln obtained from the calculations are presented in Fig. 6. From the obtained values it could be concluded:

- the high molar fraction of Na_2SO_4 in the condensed phase favours dissociation of the gaseous sulphate to $\text{Na}(\text{g})$, an opposite trend is observed for high concentration of potassium sulphate, that vaporizes mostly in form of $\text{K}_2\text{SO}_4(\text{g})$,
- since the $\text{K}_2\text{SO}_4(\text{g})$ partial pressure is independent of $p(\text{O}_2)$ and $p(\text{SO}_2)$, the whole SO_2 mass transport in the gas is enhanced in form of K_2SO_4 increasing the sulphate circulation in cement production process,
- the partial pressure of $\text{NaKSO}_4(\text{g})$ is in practice independent of the $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$ molar ratio and of the O_2 and SO_2 partial pres-

ures. The $p(\text{NaKSO}_4)$ value makes up to 30–40 % of the $p(\text{SO}_2)$ and contributes significantly to the SO_2 mass transported via gas.

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