

Knudsen Cell Mass Spectrometry of Slags and Silicates.

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Abstract.

A new approach to the Knudsen mass spectrometry of condensed matter with low vapour pressure has been developed. To obtain measurable vapour pressures in convenient temperature range, Ta, Nb, Mo, *etc*, or CaF₂ were added to the samples. The metals reduced the oxide components to gaseous suboxides. Calcium fluoride initiated exchange reactions resulting in formation of gaseous fluorides. Methods of mass spectra assignment and activity calculation are described. To overcome the relative character of vapour pressure measurements, double-cell effusion blocks were used in experiments, one cell being filled with a reference substance. Other methods of overcoming this disadvantage were proposed on the basis of simultaneous measurements of the current of representative ionic species at different temperatures over samples of different compositions. Several types of experiments have been devised to control the state of equilibrium in the effusion cell.

Introduction.

Experimental techniques most frequently used for thermodynamic studies of molten slags and silicates like EMF and heterogeneous equilibria methods have many disadvantages. The most important are uncertainties connected with electrode reactions and secondary reactions that usually proceed simultaneously with the main process and influence the composition of the substance under investigation or/and the composition of gaseous phase. Knudsen effusion technique is free from these disadvantages and in combination with mass spectrometric analysis of evaporated products allows one to determine activities of all, or at least majority of the components of multicomponent mixtures. However, its application to liquid slags is often limited by extremely low partial vapour pressure of these substances in the temperature range most suitable for the technique. It is possible to overcome the above difficulty by initiating in the effusion cell reactions producing volatile substances. The idea was realised in recent years by reducing oxide components of slags to volatile suboxides, or by adding to samples calcium fluoride, which brought about exchange reactions resulting in formation of gaseous fluorides [1-12]. Besides, addition of CaF₂ provided a possibility of studying thermodynamics

of slags, similar to the $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3\text{-SiO}_2$ melt, which play a key role in metallurgy. In this way representative files of experimental data, containing several hundred to several thousand values of activity of all components in wide temperature and concentration ranges, were obtained for molten slags and silicates of various nature and complexities. These results will be presented at the conference in special report [13]. This paper is concerned with distinguishing features of the Knudsen mass spectrometry, which made it possible to carry out extensive studies of metallurgical slags and silicate both in liquid and solid states.

Experimental arrangement.

Experimental arrangement for realisation in an effusion cell of reaction producing volatile substances was set up on the basis of the MI-1201V mass-spectrometer equipped as described in work [14]. The simplified scheme of the effusion block is given in Fig. 1. It consists of a furnace shell made of niobium (5), inside of which the effusion cell is placed. Just below the effusion cell there is thermocouple block (4), in which the hot junction of the Pt-Pt/10 % Rh thermocouple is located. A tungsten-filament heater (3), insulated by alumina, is wound directly around the furnace shell and is surrounded by radiation shields on all sides (7). The furnace shell is fastened to a special support by molybdenum screws. To decrease the heat loss, the effusion block is supported on a ceramic pedestal (6). The effusion block is placed into the water-cooled jacket (8) with the cover (11). The latter protects the elements of the ionisation region from heating. A slot in the cover of the water-cooled jacket is co-axial with the inlet slot of the ionising chamber through which the molecular beam passes. To separate the beam and background signals, a moving shutter of special configuration was used. No creeping of the substance from the effusion hole was observed. All investigations were carried out in double effusion cells, one compartment of each cell being filled with a sample and the other with a reference substance. They were made from vacuum-melted, high-purity tantalum, niobium, molybdenum, or nickel. In order to control the state of equilibrium inside the cells during experiments the orifice diameter was varied in range of ~ 0.14 to ~ 0.53 mm while the cells diameter (6 mm) and other dimensions were the same. When necessary, a correction for non-ideality of the effusion holes was introduced. Depending on the nature of samples investigated, super-high-purity iron ($<10^{-6}$ % impurities), silver (99.99 %), nickel (99.98 %), copper (99,999%), or SrF_2 of high-purity grade were used as references substances. Calibration of the thermocouple was based on the melting points of silver, copper, terbium and CaF_2 . The maximum correction for temperature did not exceed 8 K. The mass-spectra were taken using ionising energy of 50-70 eV and an acceleration voltage of 3.2 kV. Measurements of the ion current were made by means of an electrometer amplifier. The

temperature dependencies of the ion currents (vapour pressures) of the reference substances were reproducible in all cases and in good agreement with the databank of thermodynamic values IVTANTERMO [15].

The partial pressure of the vapour species were calculated according to the equation

$$p(i) = k \left(\sum_j I(i, j) \right) / \sigma(i) \quad (1)$$

where k is the mass-spectrometer sensitivity constant determined from the vapour pressure of a reference substance; $\sigma(i)$ is the cross-section of ionisation of an i -type; $\sum_j I(i, j)$ is the sum of intensities of ion currents $I(j)$ resulting from ionisation of molecules i . This equation transforms into another form, if experiments are carried out in double effusion cells

$$p(x) = p(s) \{ [\sigma(s)I(x)] / [\sigma(x)I(s)] \}. \quad (1')$$

Here x designates the substance under study and s – reference substance.

Reduction experiments.

Theoretical basis.

The theoretical basis of this experimental approach can be described by the example of the MnO-SiO₂ system. If some reductant, Me, is added to the studied mixture, the following reactions are possible:



The equilibrium constants of these reactions are equal

$$\begin{aligned} K_p(2) &= \frac{p(\text{MeO}_n) [p(\text{Mn})]^n}{[a(\text{MnO})]^n a(\text{Me})} = \frac{p^\circ(\text{MeO}_n) [p^\circ(\text{Mn})]^n}{a(\text{Me})} \\ K_p(3) &= \frac{p(\text{MeO}_n) [p(\text{SiO})]^n}{[a(\text{SiO}_2)]^n a(\text{Me})} = \frac{p^\circ(\text{MeO}_n) [p^\circ(\text{SiO})]^n}{a(\text{Me})}, \end{aligned} \quad (4)$$

where superscript “o” refers to mixtures with activities of MnO and SiO₂ equal to unity. As in all cases $a(\text{Me}) = 1$, eqn. (4) permits us to calculate the activities of manganese and silicon oxides from the partial pressures of Mn, SiO and the reductant suboxides measured over mixtures saturated and unsaturated with MnO and SiO₂:

$$\begin{aligned}
[a(\text{MnO})]^n &= \frac{p(\text{MeO}_n)[p(\text{Mn})]^n}{p^\circ(\text{MeO}_n)[p^\circ(\text{Mn})]^n} = \frac{I(\text{MeO}_n^+)[I(\text{Mn}^+)]^n}{I^\circ(\text{MeO}_n^+)[I^\circ(\text{Mn}^+)]^n} \\
[a(\text{SiO}_2)]^n &= \frac{p(\text{MeO}_n)[p(\text{SiO})]^n}{p^\circ(\text{MeO}_n)[p^\circ(\text{SiO})]^n} = \frac{I(\text{MeO}_n^+)[I(\text{SiO}^+)]^n}{I^\circ(\text{MeO}_n^+)[I^\circ(\text{SiO}^+)]^n}
\end{aligned} \quad (5)$$

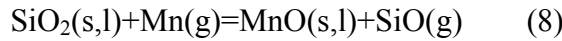
Here I and I° are the intensities of the corresponding ion currents. There is another method of determining activities which requires less experimental information. Eqn. (5) allows us to derive the following expression:

$$\left(\frac{a(\text{MnO})}{a(\text{SiO}_2)} \right)^n = \frac{[p^\circ(\text{MeO}_n)]^n}{p^\circ(\text{MeO}_n)} \left(\frac{p(\text{Mn})p^\circ(\text{SiO})}{p^\circ(\text{Mn})p(\text{SiO})} \right)^n \quad (6)$$

where $[p^\circ(\text{MeO}_n)]'$ and $p^\circ(\text{MeO}_n)$ are partial pressures over the MnO-SiO₂ mixtures saturated with SiO₂ and MnO, respectively. The relations $p^\circ(\text{MeO}_n) = K_P(2)/[p^\circ(\text{Mn})]^n$ and $[p^\circ(\text{MeO}_n)]' = K_P(3)/[p^\circ(\text{SiO})]^n$, which are valid for the saturated mixtures, transform eqn. (6) into

$$\frac{a(\text{MnO})}{a(\text{SiO}_2)} = \frac{p(\text{Mn})}{p(\text{SiO})} \sqrt[n]{K_P(3)/K_P(2)} = \frac{\sigma(\text{SiO})I(\text{Mn}^+)}{\sigma(\text{Mn})I(\text{SiO}^+)} \sqrt[n]{K_P(3)/K_P(2)}, \quad (7)$$

where $\sigma(I)$ are the ionisation cross-sections. The ratios $a(\text{MnO})/a(\text{SiO}_2)$, obtained in this way depend neither on the value of n nor on the choice of reductant because $\sqrt[n]{K_P(3)/K_P(2)}$ is equal to the equilibrium constant of the reaction



The ratio $a(\text{MnO})/a(\text{SiO}_2)$ permits us to obtain the thermodynamic functions of both the solid compounds and the liquid solutions through the partial characteristics of the components. For example, the partial Gibbs energy of manganese oxide in the heterogeneous mixtures MnO•SiO₂+SiO₂ and MnO•SiO₂+MnO•2SiO₂ can be expressed as follows:

$$\Delta G'(\text{MnO}) = RT \ln \frac{a'(\text{MnO})}{a'(\text{SiO}_2)} = RT \ln \left[K_P(8) \frac{\sigma(\text{SiO})I'(\text{Mn}^+)}{\sigma(\text{Mn})I'(\text{SiO}^+)} \right], \quad (9)$$

$$\Delta G''(\text{MnO}) = \frac{RT}{2} \left[2 \ln \left[K_P(8) \frac{\sigma(\text{SiO})}{\sigma(\text{Mn})} \right] + \ln \frac{I''(\text{Mn}^+)}{I''(\text{SiO}^+)} + \ln \frac{I'(\text{Mn}^+)}{I'(\text{SiO}^+)} \right]. \quad (10)$$

Here superscripts ' and '' refer to the heterogeneous equilibrium fields MnO•SiO₂+SiO₂ and MnO•SiO₂+MnO•2SiO₂, respectively. Similar equations can naturally be derived for the partial Gibbs energies of SiO₂. The activities of the components in the MnO-SiO₂ melt can

also be expressed through ratios of the Mn^+ and SiO^+ ion currents. Following Belton and Fruehan [16] and taking into account equation (7), we can express the MnO activities in the form:

$$\begin{aligned} \ln a(\text{MnO}) &= - \int_{x(\text{MnO})=1}^{x(\text{MnO})} x(\text{SiO}_2) d \ln \frac{a(\text{SiO}_2)}{a(\text{MnO})} = - \int_{x(\text{MnO})=1}^{x(\text{MnO})} x(\text{SiO}_2) d \ln \left(K_P (8) \frac{\sigma(\text{SiO})I(\text{Mn}^+)}{\sigma(\text{Mn})I(\text{SiO}^+)} \right) \\ &= - \int_{x(\text{MnO})=1}^{x(\text{MnO})} x(\text{SiO}_2) d \ln \left(\frac{I(\text{Mn}^+)}{I(\text{SiO}^+)} \right) \quad (11) \end{aligned}$$

This relationship contains the most reliable experimental characteristic, the ratio of the ion currents, and requires neither the ionisation cross-sections of the molecules observed in the vapour, nor the sensitivity constants of the mass spectrometer. A similar equation can, of course, be written for the calculation of SiO_2 activities.

Experimental realisation and assignment of mass spectra.

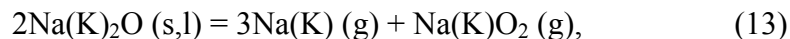
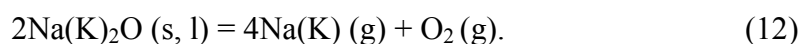
Depending on the system under study, niobium, tantalum, molybdenum, nickel or aluminium were chosen as reductants. The first four were used as cell materials and in some experiments powder of these metals was also mixed with test substances. Aluminium served only as powder which was added the samples. Random chemical analysis showed that the concentration of the reductant oxides in the test substances after the experiments was insignificant (<0.05%).

Niobium and molybdenum were selected for study of the MnO-SiO₂ system [6]. Mn^+ , SiO^+ , NbO^+ , NbO_2^+ , MoO^+ , MoO_2^+ and MoO_3^+ ions have been detected in the mass spectra of the saturated vapour. They originated from Mn, SiO, NbO, NbO₂, MoO, MoO₂, and MoO₃ produced by reaction between manganese and silicon oxides and the effusion cell materials according to eqn. (2) and (3). The Mn^+ , SiO^+ , NbO_2^+ and MoO_2^+ peaks were the most intense. The ion-current intensities of Mn^+ and SiO^+ were measured over all the samples. Both these ions are molecular and appear owing to ionisation of Mn and SiO. Both equations (5) and (11) have been applied for activity calculations (Table 1). The complete ion currents for ions originating from NbO, NbO₂, MoO, MoO₂ and MoO₃ or parts of these currents were used in equation (5), as in any case the total or partial ionisation cross-sections cancelled out. The ion-current intensities were reduced to the same sensitivity constant of the mass spectrometer with the help of the measured ion-current intensities of the reference substances. If the total ion currents were employed in equation (5), it was, of course, necessary to decode the mass-spectral lines. Standard practice founded on the independence of the equilibrium constants of some gaseous reactions from pressure was applied for this purpose. However, decoding was

not required if activities were calculated from the ion-current intensities of Mn, SiO, NbO₂ and MoO₃. The complete ion currents that originated from Mn and SiO were used for the determination of $a(\text{MnO})/a(\text{SiO}_2)$, as ionisation of each of these molecules produces ions of a single type only.

In experiments with the CaO-Al₂O₃-SiO₂ melt only SiO⁺, MeO₂⁺, MeO⁺ (Me=Ta, Nb, Mo) and MoO₃⁺ were detected in the mass spectra of the saturated vapour. This means that only silicon dioxide was reduced according to equation (3) [8]. On the contrary, no peaks connected with the products of reduction of silicon dioxide were detected in the mass spectra in the experiments with Na₂O-SiO₂ (Me=Ta, Nb, Mo, Ni) and K₂O-SiO₂ (Me=Ta, Nb, Mo, Ni, Al) mixtures [10,11]. Thus, only alkali oxides reacted with Me in the effusion cell.

Assignment of the lines connected with ionisation of molecules originated from alkali oxides: Na⁺, Na₂O⁺, NaO⁺, K⁺, K₂O⁺, KO⁺, O₂⁺ was complicated by non-uniqueness of the mechanism of their vaporisation. A recent research [17] revealed that molecules NaO₂ and similar molecules of other alkali metals were quite stable in gaseous phase and their concentration in the vapour over alkali oxides could be high enough. This means that two reactions might occur at vaporisation of Na₂O and K₂O



Owing to the two mechanisms of evaporation, the ion currents Na⁺ or K⁺ could originate from two sources, namely from ionisation of Na and NaO₂ or K and KO₂. O₂⁺ could also have two precursors, O₂ and NaO₂ or KO₂, though the major source should be NaO₂ or KO₂. Formation of NaO⁺, or KO⁺ ions through dissociative ionisation of NaO₂, or KO₂ seems very unlikely. Therefore, appearance of O₂⁺ lines in the mass spectra, like in the experiments with Mo or Ni cells, could be considered as indication that Na⁺, or K⁺ ions originated from both above sources. On the contrary, the absence of the O₂⁺ in the mass spectra in experiments with Ta or Nb cells showed that the concentration of Na(K)O₂ in the vapour was very low and Na(K)⁺ ions originated from a single source, reaction (12).

To verify these conclusions some samples of the same composition, or belonging to the same two-phase equilibrium field, were studied in the effusion cells, made from all four materials. These experiments revealed that, if Nb, or Ta cells were used, the measured vapour pressures of Na or K differed by the factor of 1.6 to 1.7, but $a(\text{Na}_2\text{O})$ or $a(\text{K}_2\text{O})$ calculated by means of equation (2) agreed within the experimental errors (1-3%). However, the vapour pressures measured, using Mo and Ni cells, resulted in significantly higher values of the alkali metals activity evidently because of activation of the second mechanism of Na(K)₂O

vaporisation and a substantial contribution into the Na(K)^+ current of Na(K)^+ ions formed by the dissociative ionisation Na(K)O_2 . To estimate the values of this contribution, the residual oxygen in the mass spectrometer was frozen out by liquid nitrogen, using a trap placed near the ion source and cooling the Knudsen block jacket. Then measurements of the O_2^+ signal connected with reaction (13) were carried out. The results made it possible to assess accurately the relationship between the Na(K)^+ and O_2^+ ion currents originating from ionisation of Na(K)O_2 molecules. The following equations were used for the purpose:

$$I[\text{Na(K)}^+, \text{Na(K)O}_2] = bI[\text{O}_2^+, \text{Na(K)O}_2] = bI(\text{O}_2^+), \quad (14)$$

$$I[\text{Na(K)}^+, \text{Na(K)}] = I[\text{Na(K)}^+] - I[\text{Na(K)}^+, \text{Na(K)O}_2] = I[\text{Na(K)}^+] - bI(\text{O}_2^+), \quad (15)$$

where b is the mass spectrum constant, $I[\text{Na(K)}^+]$ and $I(\text{O}_2^+)$ are the ion currents, measured in the above experiments. As the intensity of the type (2) reaction depended on the nature of the reductant Me, it was possible to calculate the b value from the equilibrium constant of the reaction (13) and the ion currents of the vapour species measured over the samples of the same composition in Mo and Ni cells. At the ionising energy of 50 eV the constant b was found to be equal to 1.72 and 2.90 for Na_2O and K_2O , correspondingly, depending on neither sample composition nor temperature. In the cases, when $I(\text{O}_2^+)$ were reliably established, the application of this b value to corrections of the Na(K)^+ currents measured with the help of Mo and Ni effusion cells resulted in $a(\text{Na}_2\text{O})$ and $a(\text{K}_2\text{O})$ coinciding, within the experimental uncertainties, with those found using Nb and Ta cells. The results of the experiments with Mo and Ni effusion cells were used for $a(\text{Na}_2\text{O})$ and $a(\text{K}_2\text{O})$ determinations only when it was possible to obtain reliable values of $I(\text{O}_2^+)$, that is when it was possible to divide $I(\text{Na}^+)$ and $I(\text{K}^+)$ into the two constituents discussed.

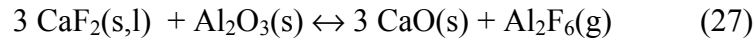
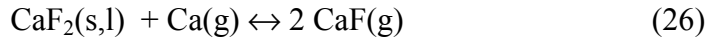
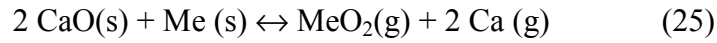
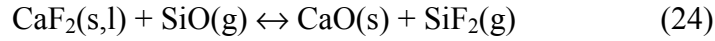
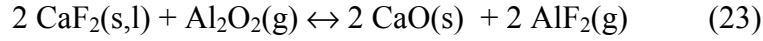
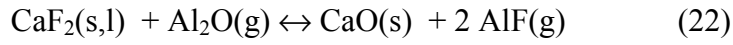
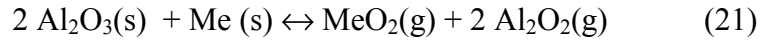
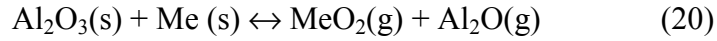
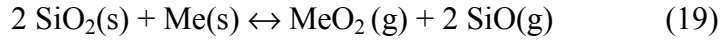
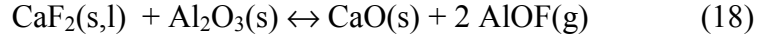
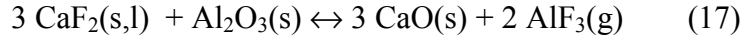
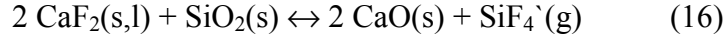
Fig. 2 illustrates that the thermodynamic values, found as describe above in experiments with effusion cells of different materials and various orifice areas and in experiments with samples of different composition in the same heterogeneous region, were in good agreement. This result confirms the existence of equilibrium in the effusion cell during experiments and proves the reliability of the thermodynamic information acquired.

Exchange reactions method

Theoretical basis.

The method founded on initiation of exchange reactions was applied to the systems where the reduction technique have failed to produce volatile suboxides with measurable vapour pressure so that it was possible to obtain activity of only a limited number of components (CaO-SiO_2 , $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$) or could not possible to determine activities at all ($\text{Al}_2\text{O}_3\text{-CaO}$). Calcium fluoride was inserted directly into the effusion cell together with slag components, or

preliminary smelted samples. Its reactions with the slag components in the most complicated system studied (CaO-Al₂O₃-SiO₂) and reactions of slag with the cell materials (Me=Ta, Nb, Mo) can be described as follows:



Very high intensity of some of the reactions (16)-(28) allowed us to use the isothermal-evaporation method along with determination of the component vapour pressures as functions of temperature. Analysis of the melt-composition changes that occurred during the isothermal-evaporation experiments was performed by integrating the time functions of the partial pressures of the saturated vapour species:

$$\begin{aligned} n(i) &= S_{eff} (2\pi RT M(i))^{-1/2} \int p(i) dt \\ &= (k/\sigma_i) \alpha S_{eff} (2\pi RT M(i))^{-1/2} \int T^{1/2} \sum_j I(i, j) dt \end{aligned} \quad (29)$$

where $n(i)$ is the amount of substance of an effusing component ($i=\text{SiF}_4, \text{SiF}_2, \text{CaF}_2, \text{CaF}, \text{Ca}, \text{Al}_2\text{F}_6, \text{AlF}_3, \text{AlF}_2, \text{AlOF}, \text{SiO}, \text{or MeO}_2$) of molar mass $M(i)$, $S_{eff} = \pi D_{eff} h/4$ is the effective effusion area (h is Klauising's coefficient). The amounts of substance of the components in the sample under investigation was expressed as follows:

$$\begin{aligned} n(\text{CaF}_2) &= n^o(\text{CaF}_2) - n^{ev}(\text{CaF}_2) - 2n(\text{SiF}_4) - n(\text{SiF}_2) - 3/2n(\text{AlF}_3) - n(\text{AlF}_2) - 1/2n(\text{AlF}) - 1/2n(\text{AlOF}) - \\ &\quad - 1/2n(\text{CaF}) - 3n(\text{Al}_2\text{F}_6), \end{aligned} \quad (30)$$

$$n(\text{SiO}_2) = n^o(\text{SiO}_2) - n(\text{SiF}_4) - n(\text{SiO}) - n(\text{SiF}_2), \quad (31)$$

$$n(\text{Al}_2\text{O}_3)=n^o(\text{Al}_2\text{O}_3)-n(\text{Al}_2\text{F}_6)-1/2[n(\text{AlF}_3)+n(\text{AlF}_2)+n(\text{AlF})+n(\text{AlOF})] \quad (32)$$

$$n(\text{CaO})=n^o(\text{CaO})+2n(\text{SiF}_4)+n(\text{SiF}_2)+3/2n(\text{AlF}_3)+n(\text{AlF}_2)+1/2n(\text{AlF})+1/2n(\text{AlOF})+ \\ +3n(\text{Al}_2\text{F}_6)-n(\text{Ca})-1/2n(\text{CaF}), \quad (33)$$

where $n^o(i)$ are the initial amounts of substance, $n^{ev}(\text{CaF}_2)$ is the amount of substance of evaporated calcium fluoride. While the initial mixture of the ingredients was heated, the continuous control of the ion currents, caused by ionisation of molecules effusing through the orifice, was carried out. This allowed calculation of the component's mole fractions in samples at the beginning of any experiment with an accuracy of ± 0.0001 to ± 0.0002 unattainable by conventional preliminary melting of samples and their subsequent chemical analysis.

Of all components of the $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3\text{-SiO}_2$ melts only the activities of CaF_2 could be calculated straightforwardly as the ratios of the vapour pressures over the liquid solution and pure calcium difluoride. Two ways were devised to determine the activities of the three other components. One was based on making use of the equilibrium constants of the reactions (16) to (27), or their combinations, which could be calculated using the information from the IVTANTERMO databank [15]. For example, when $p(\text{SiF}_4)$, $p(\text{AlF}_3)$ and $p(\text{AlOF})$ were measured, activities of CaO , Al_2O_3 and SiO_2 were determined from the following system of equations:

$$\begin{aligned} \ln\{K_p(16)/P_p\} &= 2\ln\{p(\text{CaO})\} + \ln\{p(\text{SiF}_4)\} - 2\ln\{p(\text{CaF}_2)\} - \ln\{p(\text{SiO}_2)\} \\ \ln\{K_p(17)/P_p\} &= 2\ln\{p(\text{AlF}_3)\} + 3\ln\{p(\text{CaO})\} - 3\ln\{p(\text{CaF}_2)\} - \ln\{p(\text{Al}_2\text{O}_3)\} \\ \ln\{K_p(18)/P_p\} &= \ln\{p(\text{CaO})\} + 2\ln\{p(\text{AlOF})\} - \ln\{p(\text{CaF}_2)\} - \ln\{p(\text{Al}_2\text{O}_3)\}. \end{aligned} \quad (34)$$

If one of the pressures listed happened to be immeasurable, then the corresponding equation could be replaced by another relationship, for example by equation following from reaction (19)

$$\ln\{K_p(19)/P_p\} = 2\ln\{p(\text{SiO})\} + \ln\{p(\text{SiO}_2)\} - 2\ln\{p(\text{SiO}_2)\} \quad (35)$$

Of course, if $p(\text{SiO})$ was measured, equation (5) and the data obtained in experiments with melts saturated and unsaturated with silicon dioxide can also be used for calculation of $a(\text{SiO}_2)$.

The second method of activity determination was based on the Gibbs-Duhem equation. Combination of this equation with the complete differentials of the equilibrium constants of the reaction (16) and (17) results in relations [8,12]:

$$d \ln \{a(\text{CaO})\} = \frac{2x(\text{SiO}_2) + 3x(\text{Al}_2\text{O}_3) + x(\text{CaF}_2)}{y} d \ln \{p(\text{CaF}_2)\} - \frac{x(\text{SiO}_2)}{y} d \ln \{p(\text{SiF}_4)\} - \frac{2x(\text{Al}_2\text{O}_3)}{y} d \ln \{p(\text{AlF}_3)\} \quad (36)$$

$$d \ln \{a(\text{Al}_2\text{O}_3)\} = -3 \frac{x(\text{CaF}_2) + x(\text{CaO})}{y} d \ln \{p(\text{CaF}_2)\} - \frac{3x(\text{SiO}_2)}{y} d \ln \{p(\text{SiF}_4)\} + \frac{2(x(\text{CaO}) + 2x(\text{SiO}_2))}{y} d \ln \{p(\text{AlF}_3)\} \quad (37)$$

$$d \ln \{a(\text{SiO}_2)\} = -2 \frac{x(\text{CaF}_2) + x(\text{CaO})}{y} d \ln \{p(\text{CaF}_2)\} + \frac{x(\text{CaO}) + 3x(\text{Al}_2\text{O}_3)}{y} d \ln \{p(\text{SiF}_4)\} - \frac{4x(\text{Al}_2\text{O}_3)}{y} d \ln \{p(\text{AlF}_3)\}, \quad (38)$$

which connect activities of CaO, Al₂O₃ and SiO₂ with values measured in experiments. Here $y = x(\text{CaO}) + 2x(\text{SiO}_2) + 3x(\text{Al}_2\text{O}_3)$. Similar equations can naturally be derived for partial pressures of any three vapour species. It is convenient to carry out integration of equations of the type (36)-(38) along the lines of melt composition change during isothermal evaporation, because along these lines the partial pressures of vapour species are measured in isothermal-evaporation experiments. The values of the components' activities at the initial point of integration are to be found by the first method. If in some experiments the isothermal exposure leads to a shift of the configuration point of melt composition from the region of the liquid phase stability into a heterogeneous field, the initial values of the components' activities can be calculated from the conditions of equilibrium between the liquid solution and solid compounds.

Assignment of the mass spectra lines.

The experimental method under consideration resulted in very complicated mass spectra. For example, the following ions were detected while studying the CaF₂-CaO-Al₂O₃-SiO₂ system [8]: SiF₃⁺, SiF₂⁺, SiF⁺, CaF₂⁺, CaF⁺, Ca⁺, Al₂F₅⁺, AlF₃⁺, AlF₂⁺, AlF⁺, Al⁺, AlOF⁺, SiO⁺, MeO⁺, MeO₂⁺ (Me=Nb, Ta, Mo – effusion cell materials) and MoO₃⁺. The solution of the mass-spectra assignment problem was found in the context of the method, based on independence of some gaseous reactions on pressure, even for the case of double and triple lines, when there were no two non-overlapping lines [1,2,18].

It is convenient to describe the method by the example of the CaF₂-Al₂O₃-CaO system, components of which are connected by reactions (17) and (18) [1,2,4]. The Al₂F₅⁺, AlF₃⁺, AlF₂⁺, AlF⁺, Al⁺, AlOF⁺, CaF₂⁺, CaF⁺ and Ca⁺ were registered in the mass spectra of saturated vapour over the studied compositions. The Al₂F₅⁺ ions are fragmentary, formed by

the ionisation of dimer molecules of aluminium trifluoride. The AlF_3^+ ions are molecular, originating from AlF_3 . The AlF_2^+ ions can be molecular, originating from AlF_3 , or fragmentary, formed by dissociative ionisation of aluminium trifluoride molecules. The AlF^+ ions can have three precursors: AlF_3 , AlF_2 (fragment ions) and AlF (molecular ions). All aluminium fluoride molecules (AlF_3 , AlF_2 , AlF) can be sources of the fragmentary Al^+ ions. The AlOF^+ ions are molecular, originating from molecules of aluminium oxide fluoride. In order to account for appearance of AlF_2 and AlF molecules in the vapour, the equilibrium constants of all independent reactions that might occur in the effusion cell were calculated, using the IVTANTERMO data [15]. The calculation revealed that aluminium fluoride and difluoride can be produced by reactions between aluminium suboxide and calcium difluoride as the equilibrium constants of these reactions are greater than unity. Al_2O , Al_2O_2 and AlO are the products of reduction of Al_2O_3 by the effusion-cell materials, the reducing capability increasing in the series $\text{Mo} < \text{Ni} < \text{Ta} < \text{Nb}$. Depending on the activity of the components of the $\text{CaF}_2\text{-Al}_2\text{O}_3\text{-CaO}$ system, the above reactions can result in $p(\text{AlF})$ several orders of magnitude higher than the partial pressure of AlF_3 attained owing to reaction (17). The concentration of Al atoms produced in the vapour by the reactions between Al_2O_3 and the cell materials is several orders of magnitude lower than that of AlF and AlF_2 . It should be noted that direct reduction of aluminium fluorides by the cell-materials is almost negligible and should lead to the pressure of the reduced species (AlF_2 , AlF , Al) several orders of magnitude lower than those observed in reality.

Reaction



and mass spectra registered over liquid solutions and the regions of three-phase equilibria $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3 + \text{CaF}_2$, $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3 + \text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{L} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{CaO}$, $\text{L} + \text{CaO} \cdot 6\text{Al}_2\text{O}_3 + \text{CaF}_2$, $\text{L} + 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3$, $\text{L} + \text{CaO} \cdot 6\text{Al}_2\text{O}_3 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3$, $\text{L} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$, $\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + 11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ were chosen for determination of the contributions of different aluminum fluorides into the ion currents AlF_2^+ , AlF^+ and Al^+ . Over each three-phase region $p(\text{AlF}_3)$ is independent on the cell material and consequently the ion currents AlF_2^+ , AlF^+ and Al^+ , originating from ionisation of AlF_3 , should also be constant, if the sensitivity of the mass spectrometer is fixed. These currents were normalised to the same sensitivity, using two methods. One was based on the ion currents of the reference substances and the other – on the non-overlapping lines AlF_3^+ and the mass spectrum constants:

$$r_I = I(\text{AlF}_2^+, \text{AlF}_3) / I(\text{AlF}_3^+, \text{AlF}_3),$$

$$r_2 = I(\text{AlF}^+, \text{AlF}_3) / I(\text{AlF}_3^+, \text{AlF}_3), \quad (40)$$

$$r_3 = I(\text{Al}^+, \text{AlF}_3) / I(\text{AlF}_3^+, \text{AlF}_3).$$

Both methods gave coinciding results, but the first was preferred because of the low intensity of the AlF_3^+ ion current. The ratios

$$n = I(\text{AlF}^+, \text{AlF}_2) / I(\text{AlF}_2^+, \text{AlF}_2) \text{ and } l = I(\text{Al}^+, \text{AlF}_2) / I(\text{AlF}_2^+, \text{AlF}_2) \quad (41)$$

should evidently be constant. These conditions allow separation of the AlF_2^+ , AlF^+ and Al^+ ion currents into constituent parts, originating from one of the molecules AlF_3 , AlF_2 , or AlF . The true intensities of the AlF_2^+ , AlF^+ and Al^+ currents associated with the ionisation of the AlF_2 molecules can be expressed as

$$I(\text{AlF}_2^+, \text{AlF}_2) = I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3),$$

$$I(\text{AlF}^+, \text{AlF}_2) = n \times [I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)], \quad (42)$$

$$I(\text{Al}^+, \text{AlF}_2) = l \times [I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)],$$

where $I(\text{AlF}_2^+)$ is the observed intensity of the ion current. Similarly, for the AlF^+ and Al^+ ion currents produced by ionisation of the AlF molecules we have

$$I(\text{AlF}^+, \text{AlF}) = I(\text{AlF}^+) - n \times [I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)] - I(\text{AlF}^+, \text{AlF}_3),$$

$$I(\text{Al}^+, \text{AlF}) = I(\text{Al}^+) - l \times [I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)] - I(\text{Al}^+, \text{AlF}_3), \quad (43)$$

where $I(\text{AlF}^+)$ and $I(\text{Al}^+)$ are the experimentally determined intensities of the ion currents. Thus, the vapour pressures of aluminium mono-, di- and trifluorides in the effusion cell can be expressed by the equations:

$$p(\text{AlF}_3) = [kT / \sigma(\text{AlF}_3)] \times [I(\text{AlF}_3^+, \text{AlF}_3) + I(\text{AlF}_2^+, \text{AlF}_3) + I(\text{AlF}^+, \text{AlF}_3) + I(\text{Al}^+, \text{AlF}_3)], \quad (44)$$

$$p(\text{AlF}_2) = [kT / \sigma(\text{AlF}_2)] \times (1+n+l) \times [I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)], \quad (45)$$

$$p(\text{AlF}) = [kT / \sigma(\text{AlF})] \times \{I(\text{AlF}^+) + I(\text{Al}^+) - (n+l) \times [I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)] - I(\text{AlF}^+, \text{AlF}_3) - I(\text{Al}^+, \text{AlF}_3)\}. \quad (46)$$

Whatever material is chosen for the effusion cell the following equations is valid for reaction (39):

$$K_P(39) = [\sigma^2(\text{AlF}_2) / \sigma(\text{AlF}_3) / \sigma(\text{AlF})] \times \{I(\text{AlF}_3^+, \text{AlF}_3) + I(\text{AlF}_2^+, \text{AlF}_3) + I(\text{AlF}^+, \text{AlF}_3) + I(\text{Al}^+, \text{AlF}_3)\} \times \{I(\text{AlF}^+) + I(\text{Al}^+) - (n+l) \times [I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)] - I(\text{AlF}^+, \text{AlF}_3) - I(\text{Al}^+, \text{AlF}_3)\} / \{(1+n+l) \times [I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)]\}^2 \quad (47)$$

The $K_P(39)$ was calculated from the IVTANTERMO data [15] and the molecular ionisation cross-sections – from information [19] according to the additivity rule as it was indicated above. However it should be noted that the results of the calculation of the ratio $\sigma^2(\text{AlF}_2) / \sigma(\text{AlF}_3) / \sigma(\text{AlF})$ happened to be is practically equivalent to the commonly used

assumption that this ratio is equal unity for isomolecular reactions. The last equation contains five unknowns: $I(\text{AlF}_2^+, \text{AlF}_3)$, $I(\text{AlF}^+, \text{AlF}_3)$, $I(\text{Al}^+, \text{AlF}_3)$, n and l . Thus in order to interpret the mass spectra under discussion completely, it was necessary to measure the AlF_3^+ , AlF_2^+ , AlF^+ and Al^+ ion currents over a slag mixture of the same composition, using effusion cells made from five different materials. The solution of this problem was greatly simplified owing to the following experimental finding. The partial pressure of AlF over $\text{CaF}_2\text{-Al}_2\text{O}_3\text{-CaO}$ samples of the composition, belonging to the region of equilibrium with pure CaO , was almost three orders of magnitude higher than that of aluminium di- and trifluoride, thus meaning that the AlF^+ and Al^+ ion currents originated almost exclusively from AlF molecules. This allowed determination of one more mass spectrum constant,

$$m = I(\text{AlF}^+, \text{AlF}) / I(\text{Al}^+, \text{AlF}), \quad (48)$$

and one more equation, containing the same five unknowns,

$$m = \frac{I(\text{AlF}^+) - n[I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)] - I(\text{AlF}^+, \text{AlF}_3)}{I(\text{Al}^+) - l[I(\text{AlF}_2^+) - I(\text{AlF}_2^+, \text{AlF}_3)] - I(\text{Al}^+, \text{AlF}_3)}. \quad (49)$$

The last equation reduced the number of experiments with effusion cells made of different materials to three. We now have a system of six equations containing five unknowns, which can be solved, for example, by the least squares method. Adequacy of the described approach was confirmed by independence of m from the cell materials and by agreement with the results of investigation of equilibria involving aluminium fluoride reported in refs [20, 21].

The results of experiments, where the smallest differences between the intensities of AlF_2^+ , AlF^+ and Al^+ ion currents were observed, were used in equation (47). These were the experiments with samples belonging to the $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3 + \text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{L} + 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + 11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ fields at 1773, 1723 and 1650 K and to the $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3 + \text{CaF}_2$ and $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3 + \text{CaO} \cdot \text{Al}_2\text{O}_3$ at 1600 K. The constant m was established from data for the $\text{L} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{CaO}$, $\text{L} + \text{CaO}$ and $\text{L} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ region. The result of assignment given in Table 2 are in good agreement with information obtained in the studies of AlF_3 sublimation and equilibria involving aluminium mono-, di- and trifluorides [20-28]. A similar scheme was applied to interpret the CaF_2^+ , CaF^+ and Ca^+ lines.

Consideration of equilibrium conditions in effusion cells.

Two types of experiments in isothermal-evaporation technique have been devised to prove decisively that the state of equilibrium existed in the effusion cell. In the first, the mixtures of the same initial composition were evaporated from effusion cells of different

orifice areas. In the second, melts had different initial compositions chosen in such a way that their configuration points should fall on the same distillation line. The orifice diameters were the same in some instances, or different in others. In all cases, both the position of distillation lines on the phase diagram and the values of partial pressures of the vapour species were in good agreement. This is illustrated in Figs 3 and 4, where the partial pressures of the major vapour species (CaF_2 , AlF_3 , SiF_4) determined in experiments with niobium and molybdenum cells are plotted against $x(\text{CaF}_2)$.

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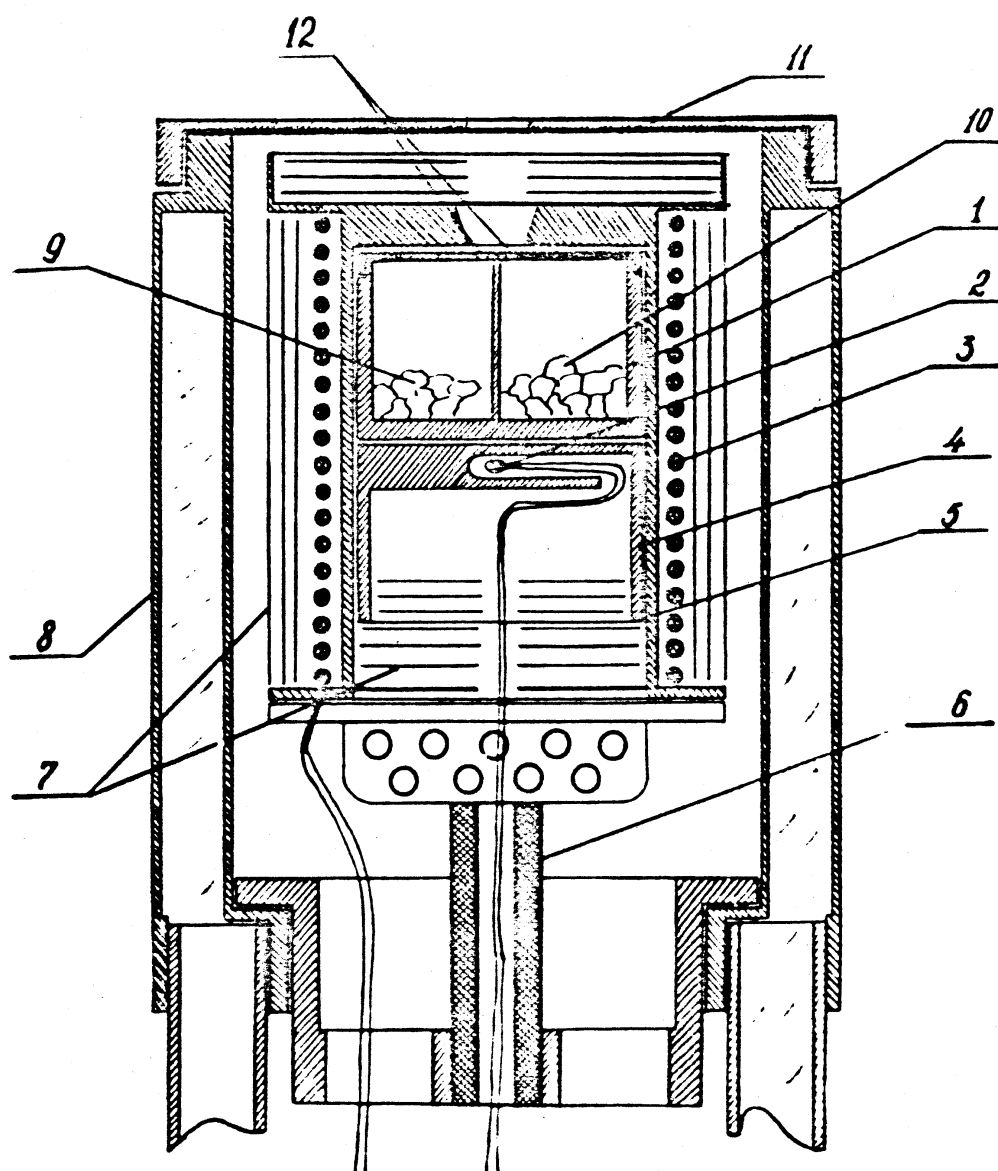


Figure 1. Schematic diagram of the effusion block: 1 – double effusion cell; 2 – Pt, Pt-10%Rh thermocouple; 3 – tungsten heating element; 4 – thermocouple block; 5 – high temperature furnace; 6 – alumina holder; 7 – radiation shields; 8 – water-cooled jacket; 9 – reference substance; 10 – substance under investigation; 11 – water-cooled jacket cover; 12 – effusion holes.

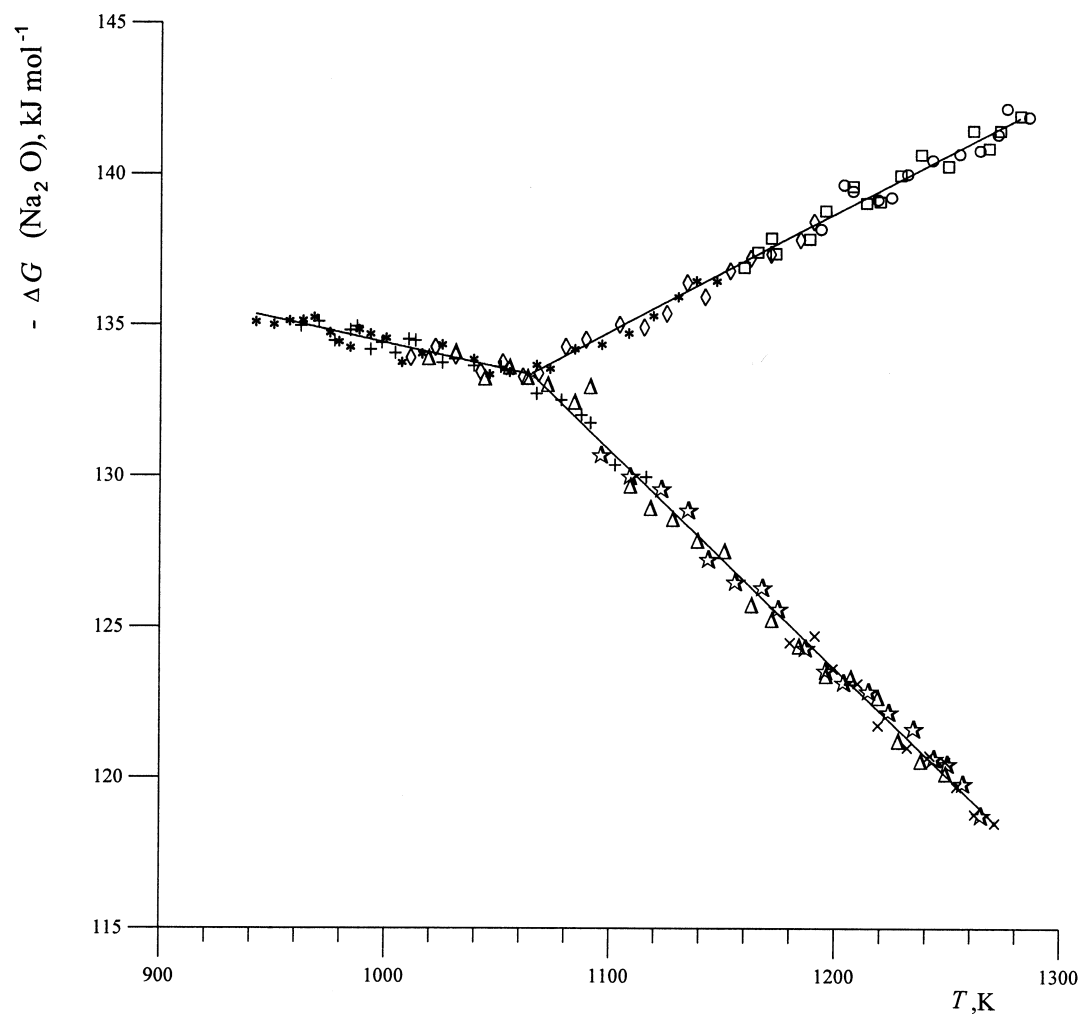


Figure 2. Temperature dependencies of the partial Gibbs energy of Na_2O in the $\text{N}_3\text{S}_2+\text{NS}$, $\text{N}_3\text{S}_2+\text{N}_2\text{S}$ and $\text{N}_2\text{S}+\text{NS}$ two-phase regions. *: $x(\text{SiO}_2)=0.477$, material of effusion cell=niobium, orifice diameter (d_{or})= 3.11×10^{-4} m; \diamond : $x(\text{SiO}_2)=0.430$, Ta, $d_{or}=2.03 \times 10^{-4}$ m; \square : $x(\text{SiO}_2)=0.450$, Mo, $d_{or}=2.07 \times 10^{-4}$ m; O: $x(\text{SiO}_2)=0.405$, Mo, $d_{or}=3.51 \times 10^{-4}$ m; +: $x(\text{SiO}_2)=0.382$, Nb, $d_{or}=2.09 \times 10^{-4}$ m; Δ : $x(\text{SiO}_2)=0.382$, Ta, $d_{or}=3.14 \times 10^{-4}$ m; \star : $x(\text{SiO}_2)=0.360$, Mo, $d_{or}=2.48 \times 10^{-4}$ m; \times : $x(\text{SiO}_2)=0.349$, Ni, $d_{or}=2.12 \times 10^{-4}$ m.

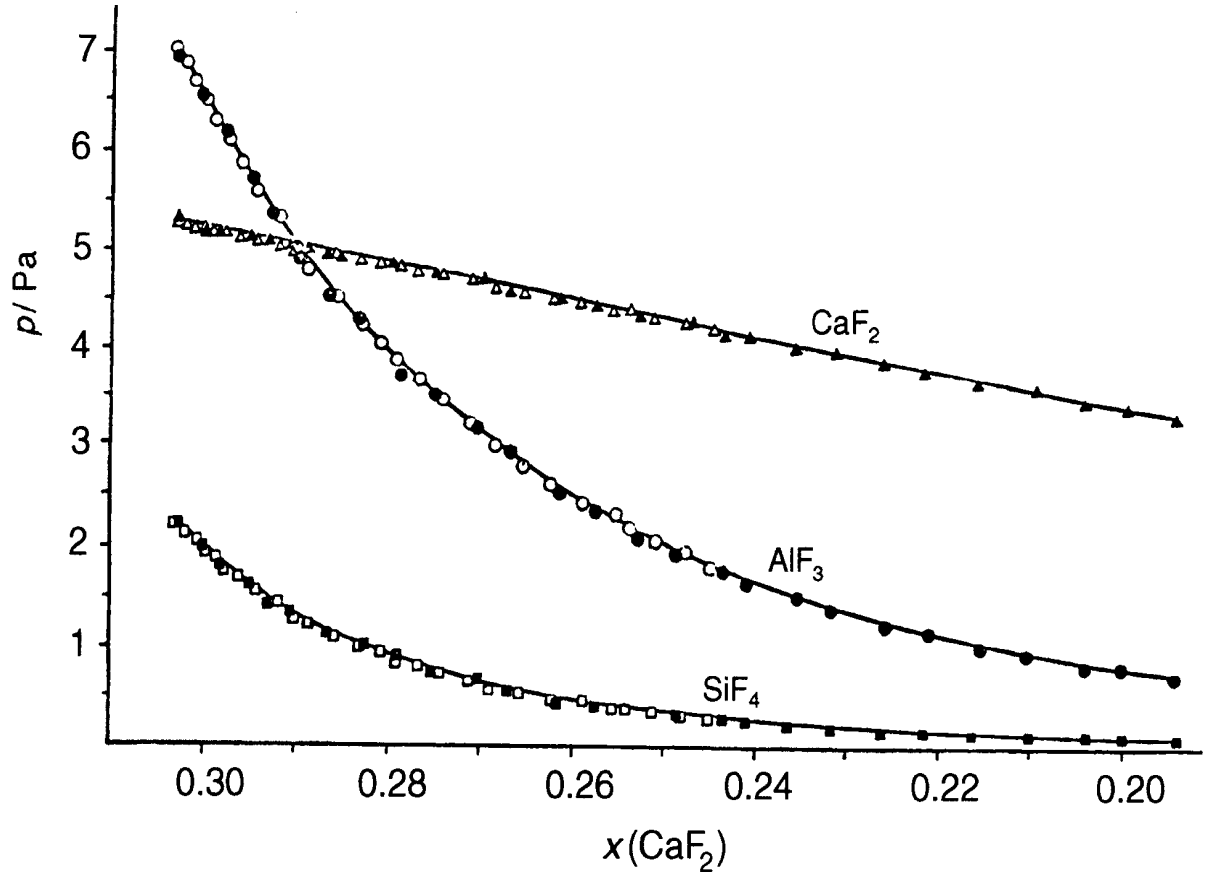


Figure 3. Vapour pressures of CaF_2 , AlF_3 and SiF_4 over the melt with initial concentrations $x^0(\text{CaF}_2)=0.303$, $x^0(\text{SiO}_2)=0.242$, $x^0(\text{Al}_2\text{O}_3)=0.147$ as a function of $x(\text{CaF}_2)$ along the distillation line during an isothermal ($T = 1673 \text{ K}$) evaporation experiment in niobium cells. Orifice diameter 2.08×10^{-4} : Δ , $p(\text{CaF}_2)$; \circ , $p(\text{AlF}_3)$; \square , $p(\text{SiF}_4)$; orifice diameter: 3.32×10^{-4} : \blacktriangle , $p(\text{CaF}_2)$; \bullet , $p(\text{AlF}_3)$; \blacksquare , $p(\text{SiF}_4)$.

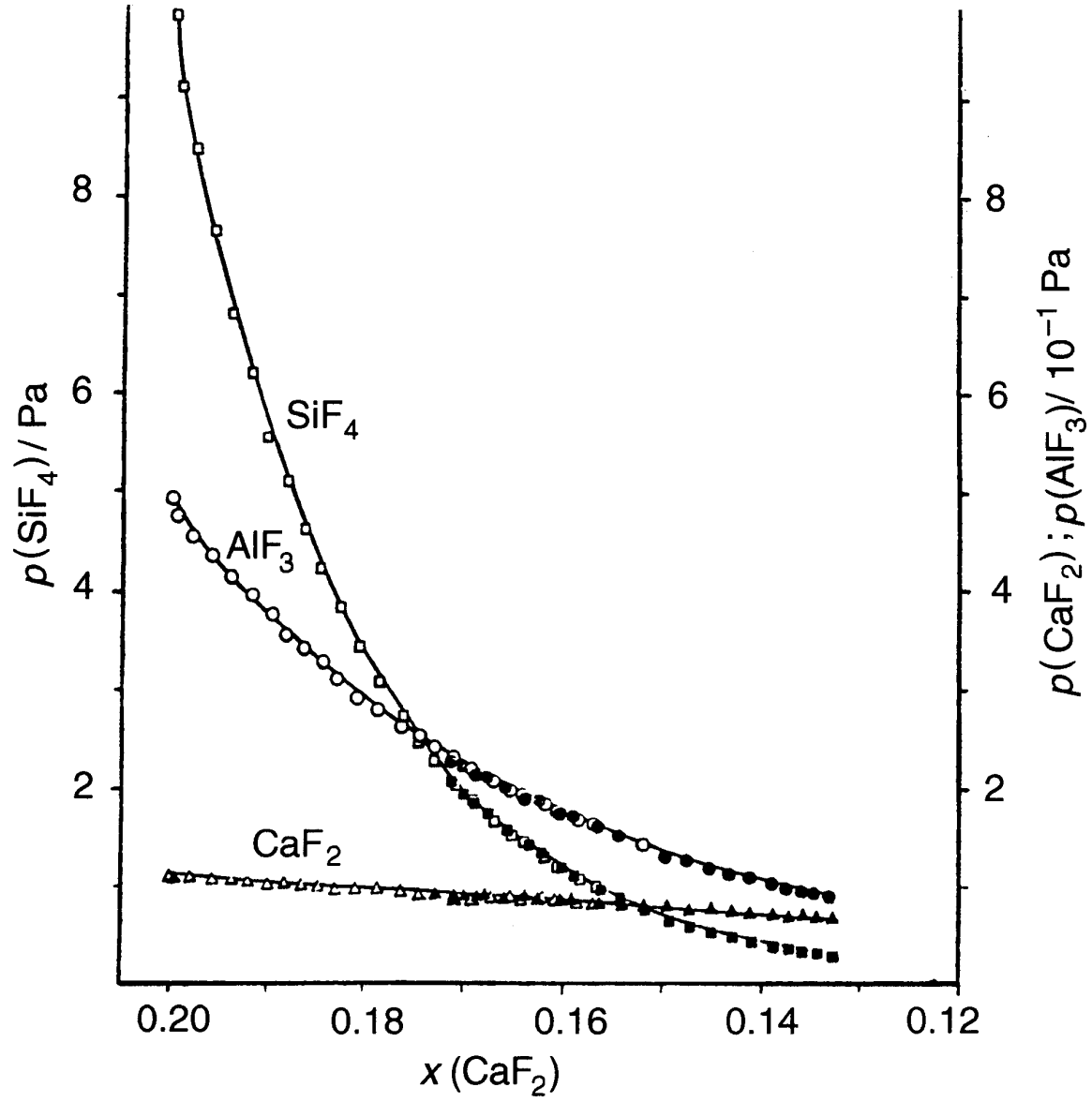


Figure 4. Vapour pressures of CaF_2 , AlF_3 and SiF_4 over the melts with initial concentrations $x^0(\text{CaF}_2)=0.201$, $x^0(\text{SiO}_2)=0.400$, $x^0(\text{Al}_2\text{O}_3)=0.095$ (open symbols) and $x^0(\text{CaF}_2)=0.171$, $x^0(\text{SiO}_2)=0.391$, $x^0(\text{Al}_2\text{O}_3)=0.096$ (full symbols) as a function of $x(\text{CaF}_2)$ along the distillation line during an isothermal ($T=1473$ K) evaporation experiment in molybdenum cells. Orifice diameter 2.54×10^{-4} : Δ , $p(\text{CaF}_2)$; \circ , $p(\text{AlF}_3)$; \square , $p(\text{SiF}_4)$; orifice diameter: 4.09×10^{-4} : \blacktriangle , $p(\text{CaF}_2)$; \bullet , $p(\text{AlF}_3)$; \blacksquare , $p(\text{SiF}_4)$.

Table 1. Activities of MnO and SiO₂ in the MnO-SiO₂ melts at 1773 K obtained in different ways (reference states – solid MnO and β -cristobalite).

$x(\text{SiO}_2)$	$a(\text{SiO}_2)$		$a(\text{MnO})$	
	Eqn. (5)	Eqn.(11)	Eqn. (5)	Eqn.(11)
0.515	0.983	0.992	0.137	0.138
0.490	0.930	0.928	0.148	0.147
0.457	0.805	0.813	0.165	0.166
0.405	0.462	0.463	0.254	0.254
0.368	0.230	0.230	0.396	0.394
0.327	0.102	0.102	0.611	0.608
0.302	0.0630	0.0635	0.754	0.756
0.273	0.0391	0.0391	0.922	0.919

Table 2. Calculated intensity of mass spectra lines (I , arbitrary units) originating from ionisation of the AlF₃, AlF₂ and AlF molecules (energy of ionising electrons 50 eV).

$T, \text{ K}$	$I(\text{AlF}_3^+)$	$I(\text{AlF}_2^+)$	$I(\text{AlF}^+)$	$I(\text{Al}^+)$	$I(\text{AlF}_2^+)$	$I(\text{AlF}^+)$	$I(\text{Al}^+)$	$I(\text{AlF}^+)$	$I(\text{Al}^+)$
	AlF ₃				AlF ₃			AlF	
1600	1.3	100	2.1	2.2	100	3.6	4.7	100	16.8
1650	1.6	100	1.9	1.9	100	4.1	4.7	100	16.2
1723	1.4	100	2.2	2.4	100	3.9	4.5	100	16.4
1773	1.4	100	2.1	2.3	100	3.9	4.9	100	17.1