Mass Spectrometric Investigations of the Evaporation of Crystalline Compounds of the System Cs_2O-Al_2O_3-SiO_2 *

Part II: The Compounds $CsAlSiO_4$ and $CsAlSi_5O_{12}$

R. Odoj ** and K. Hilpert

Institut für Chemie der Kernforschungsanlage Jülich,
Institut 4: Angewandte Physikalische Chemie

Z. Naturforsch. **35a**, 9–13 (1980); received October 16, 1979

Dedicated to Professor Dr. H. Hintenberger on his 70th birthday

The evaporation of the synthetic compounds $CsAlSiO_4$ and $CsAlSi_5O_{12}$ was studied by high temperature mass spectrometry. The measurements were carried out under equilibrium conditions with Knudsen cells in the temperature ranges 1242 to 1567 K ($CsAlSiO_4$) and 1542 to 1803 K ($CsAlSi_5O_{12}$). The obtained Cs partial pressures are given by the equations

$$\log p\,(\mathrm{Pa}) = -18\,497/T\,(\mathrm{K}) + 11.85 \quad (CsAlSiO_4) \quad \text{and}$$
$$\log p\,(\mathrm{Pa}) = -26\,974/T\,(\mathrm{K}) + 14.6 \quad (CsAlSi_5O_{12})\,.$$

The probable uncertainty of the vapor pressures is $\pm 43\%$. The following enthalpies of sublimation of Cs (g) were computed:

$$\Delta_{\mathrm{sub}} H^\circ_{1405}\,(CsAlSiO_4) = 353.6 \pm 9.8\ \mathrm{kJ\,mol^{-1}} \quad \text{and}$$
$$\Delta_{\mathrm{sub}} H^\circ_{1673}\,(CsAlSi_5O_{12}) = 516.3 \pm 18\ \mathrm{kJ\,mol^{-1}}\,.$$

The Cs partial pressures over $CsAlSiO_4$, $CsAlSi_5O_{12}$ and $CsAlSi_2O_6$ (see part I of this work [1]) are discussed with respect to their consequences for the final storage of high level radioactive waste.

1. Introduction

The volatility of the fission product cesium is one of the significant problems in nuclear technology, applying both its retention in the fuel element during the operating time of the nuclear power plant (see part I of this paper [1]) and its immobilization in glass, glass-ceramic or crystalline products for its final storage [2–4]. Therefore, the evaporation of the compound $CsAlSi_2O_6$ was studied in part I [1] of this paper to determine the diminution of the chemical activity of Cs by the formation of this compound.

In addition to the well known compound $CsAlSi_2O_6$ there are the two cesium aluminosilicates $CsAlSiO_4$ and $CsAlSi_5O_{12}$ which might also be of interest for a diminution of the chemical activity of Cs. $CsAlSiO_4$ was for the first time prepared by Barrer and McCallum [5] using hydrothermal crystallization. Solov'eva, Vydrik and Moroz [6] synthesized this compound from Cs_2CO_3, silica acid gel and $Al(OH)_3$ by sintering at temperatures above 1373 K. Klaska and Jarchow [7] also used hydrothermal crystallization for the preparation of $CsAlSiO_4$. Finally, Langlet [8] succeeded in preparing this compound by sintering mixtures of $CsNO_3$, Al_2O_3 and $SiO_2 \cdot H_2O$ between 773 and 1273 K. Contradictory crystalline structures for $CsAlSiO_4$ resulted from the aforementioned studies. The structure of $CsAlSiO_4$ was determined to be cubic [5], tetrahedral [6] and orthorhombic [7].

The compound $CsAlSi_5O_{12}$ was recently detected by Ito [9]. He observed $CsAlSi_5O_{12}$ single crystals of orthorhombic structure upon slow cooling of a melt containing Ba- and Cs-vanadate.

By preparing samples with different Al_2O_3-, SiO_2- and Cs_2O-content we tried to obtain hitherto unknown cesium aluminosilicate compounds [10]. We looked especially for a compound of the composition $Cs_2O \cdot Al_2O_3 \cdot 6\,SiO_2$ which would represent a homologue of the mineral Albit or potassium feldspar. These efforts were unsuccessfull.

No thermodynamic data about the chemical activity of Cs in $CsAlSiO_4$ and $CsAlSi_5O_{12}$ are available. Therefore, these compounds were prepared and their evaporation was studied by high temperature mass spectrometry in order to determine the potentialities of $CsAlSiO_4$ and $CsAlSi_5O_{12}$

---

* Doctoral thesis of R. Odoj, University Bonn 1977.

** Now Institut für Chemische Technologie der KFA Jülich.

Reprint requests to Dr. K. Hilpert, Institut 4: Angewandte Physikalische Chemie, Postfach 1913, D-5170 Jülich.

0340-4811 / 80 / 0100-0009 $ 01.00/0. — Please order a reprint rather than making your own copy.

for a retention of Cs in comparison with that of $CsAlSi_2O_6$.

2. Experimental

The measurements were carried out using the same mass spectrometer Knudsen cell system as it was described in part I [1]. Details are given in [11, 12, 13]. The molybdenum Knudsen cell had a knife edged effusion orifice with a diameter of 0.1 mm. The ions were generated by electron impact with an energy of 22 eV.

The temperatures were measured with an optical pyrometer on the bottom of a black body cavity laterally placed close to and below the bottom of the cylindrical Knudsen cell. A ceramic tube was attached between the inner heat shield and the opening of the black body cavity in the cell in order to avoid differential temperature errors which give rise to large errors for the slope of the vapor pressure curves and hence also for the thermodynamic data derived from it. Without ceramic tube the heat radiation from the cathode which surrounds the Knudsen cell for the heating gets into the black body cavity by reflection on the polished tantalum heat shields and causes a differential temperature error depending on the temperature difference between the cathode and the Knudsen cell. This could be shown by comparing the slope of a measured silver vapor pressure curve with that computed from the data given in the literature [14]. The differential temperature error is, however, only observable at temperatures below about 1300 K since at high temperatures the Knudsen cell is mainly heated by electron bombardment by which the temperature difference between the cell and the cathode is diminished. The aforementioned modification of the temperature measurement has been described in detail in [10].

In order to determine the vaporization of the compounds $CsAlSiO_4$ and $CsAlSi_5O_{12}$ samples of stoichiometric composition were prepared using the same preparation procedure with hydrothermal crystal growth as it was employed in part I of this paper [1] to synthesize $CsAlSi_2O_6$. The samples obtained were checked by X-ray diffraction. Both showed an orthorhombic structure [15]. The volume of the unit cell of $CsAlSi_5O_{12}$ is approximately twice the amount of the corresponding volume of $CsAlSiO_4$ [15]. For the $CsAlSiO_4$ sample all diffraction lines belong to only one phase. In contrast to that the diffraction pattern of the $CsAlSi_5O_{12}$ sample showed not only the lines of the orthorhombic $CsAlSi_5O_{12}$ structure but also those of the compound $CsAlSi_2O_6$. The coexistence of the two phases is caused by the formation of crystalline nuclei of $CsAlSi_2O_6$ during the preparation of the sample. The transformation of $CsAlSi_2O_6$ into $CsAlSi_5O_{12}$ is difficult on account of the comparatively high stability of $CsAlSi_2O_6$.

3. Results

During the evaporation of the compounds $CsAlSiO_4$ and $CsAlSi_5O_{12}$ the ions Cs^+, SiO^+ and Cs^{2+} were observed. The intensities of SiO^+ and Cs^{2+} are less than 1% in comparison with the Cs^+ intensity. The ions were identified by their mass and isotopic distribution. Ionisation efficiency measurements of Cs^+ and the appearance potentials obtained reveal that the Cs^+ is formed by single ionization.

The Cs partial pressure, p, was determined by using the equation

$$p = E\, \sigma_{Ag}/\sigma_{Cs}\ \ \gamma_{Ag}/\gamma_{Cs}\ \ I_{Cs}\, T\,, \tag{1}$$

where I is the Cs^+ ion intensity and T the Knudsen cell temperature. The terms $\sigma_{Ag}/\sigma_{Cs} = 0.47$ [1] as well as $\gamma_{Ag}/\gamma_{Cs} = 1.10$ are the ratios of the ionization cross sections and of the multiplier efficiencies. The γ_{Ag}/γ_{Cs} ratio was estimated by assuming that the multiplier efficiency is proportional to the velocity of the ions impinging on the first dynode of the multiplier. The sensitivity, E, of the Knudsen cell-mass spectrometer system was determined in the same way as it was described in part I of this paper [1] using silver for the pressure calibration.

In order to determine the Cs partial pressures over $CsAlSiO_4$ and $CsAlSi_5O_{12}$ two runs were performed for each compound. At the beginning of each measurement all samples showed the same time dependent Cs^+ ion intensity at constant temperature as it could be observed upon studying the compound $CsAlSi_2O_6$ [1]. Since the $CsAlSiO_4$ samples contain only one phase the carrying out of the measurements was analogous to that of the compound $CsAlSi_2O_6$ [1].

In contrast to that the $CsAlSi_5O_{12}$ samples contained the two phases $CsAlSi_2O_6$ and $CsAlS_2i_5O_{12}$. The Cs pressure that could be observed at the beginning of the measurement of the $CsAlSi_5O_{12}$ sample after the pressure had become constant at constant temperature, equals that determined over $CsAlSi_2O_6$ in part I [1] of this paper. After heating the sample for 50 h at 1700 K the vapor pressure decreased at the same temperature and then again became constant. Subsequently, vapor pressure curves were determined by measuring the ion intensities at different temperatures. X-ray diffraction studies of the sample after the evaporation measurement revealed that only the lines of $CsAlSi_5O_{12}$ could be detected. The loss of the $CsAlSi_2O_6$ phase is caused by the loss of Cs by effusion through the orifice and by chemical reaction of $CsAlSi_2O_6$ with the surplus of SiO_2 present in the sample forming $CsAlSi_5O_{12}$.

The Cs partial pressures obtained over $CsAlSiO_4$ and $CsAlSi_5O_{12}$ are shown in Figs. 1 and 2. Logarithmic vapor pressure temperature relationships were obtained by a least squares computation (see Table 1). The enthalpies of sublimation of Cs at the mean temperature of the measurement, T_m, are also tabulated in Table 1. They were computed from the slope of the vapor pressure curves according to the second law method by using the equation

$$\Delta_{\mathrm{sub}} H^{\circ}_{T\mathrm{m}} = -R\, d \ln p_{\mathrm{Cs}}/d(1/T)\,, \tag{2}$$

where R is the gas constant.

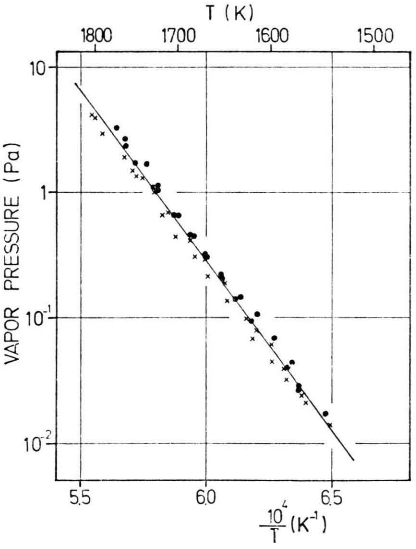

Fig. 1. Cs partial pressures over the compound $CsAlSiO_4$ (● run 1, × run 2).

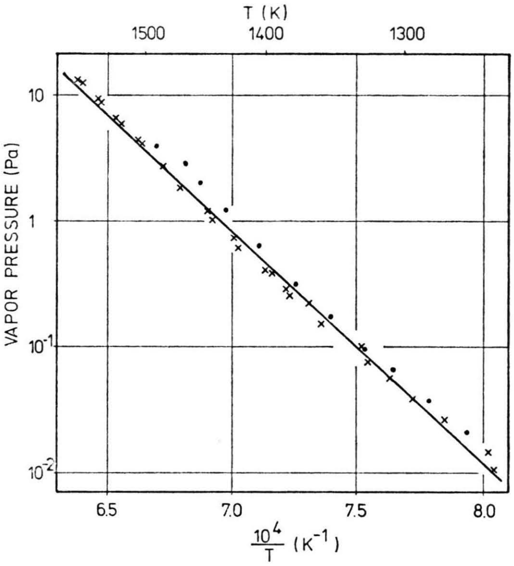

Fig. 2. Cs partial pressures over the compound $CsAlSi_5O_{12}$ (● run 1, × run 2).

4. Discussion and Conclusions

The errors indicated in Table 1 are random errors resulting from the scatter of the vapor pressure points given in Figs. 1 and 2. The estimated uncertainties of the ratio of the ionization cross sections, the ratio of the multiplier efficiencies, the sensitivity, the temperature and the ion intensities in % are ±40, ±5, ±15, ±0.5 and ±5, respectively. By employing these values a probable uncertainty of ±43% was obtained for the vapor pressure over $CsAlSiO_4$ and $CsAlSi_5O_{12}$. The probable uncertainties of the enthalpies of sublimation of Cs are ± 9.8 kJ mol^{-1} ($CsAlSiO_4$) and ± 18 kJ mol^{-1} ($CsAlSi_5O_{12}$). They were obtained by assuming the aforementioned absolute temperature error. Additionally, a differential temperature error of ±4 K at the maximum temperature, and of ∓4 K at the minimum temperature of the various runs carried out for $CsAlSiO_4$ and $CsAlSi_5O_{12}$ was taken into account.

Obviously, the vapor pressures and the heats of sublimation obtained in the two different runs for the compound $CsAlSiO_4$ agree within the accuracy of measurement. The same is true for the data of the two runs obtained on evaporating $CsAlSi_5O_{12}$.

The Cs vapor pressures over the compound $CsAlSiO_4$ were also determined by us according to the method of quantitative evaporation [16].

Table 1. Cs vapor pressure and sublimation enthalpy of Cs for $CsAlSiO_4$ and $CsAlSi_5O_{12}$.

Compound	Run	Cs pressure (p in Pa, T in K)	p_{Cs} 1450 K (Pa)	Temperature range (K)	T_m (K)	$\Delta_{sub} H^{\circ}_{Tm}$ (KJ mol^{-1})
$CsAlSiO_4$	1	$\log p = -(18439 \pm 197)/T + (11.8 \pm 2.2)$	1.21×10^{-1}	1259–1493	1376	351.5 ± 4.2
	2	$\log p = -(18554 \pm 630)/T + (11.9 \pm 2.5)$	1.27×10^{-1}	1242–1567	1405	355.6 ± 12.6
Average		$\log p = -18497/T + 11.85$	1.24×10^{-1}	1242–1567	1405	353.6
$CsAlSi_5O_{12}$	1	$\log p = -(27199 \pm 345)/T + (14.8 \pm 2.3)$	1.10×10^{-4}	1564–1803	1684	512.1 ± 6.3
	2	$\log p = -(26749 \pm 321)/T + (14.4 \pm 2.3)$	8.96×10^{-5}	1542–1769	1656	520.5 ± 6.7
Average		$\log p = -26974/T + 14.6$	9.94×10^{-5}	1542–1803	1673	516.3

The vapor pressures determined by quantitative evaporation agree within the accuracy of the measurement with those obtained in this work.

By comparing the Cs partial pressures obtained over the various cesium aluminosilicate compounds at the mean temperature of 1450 K, it follows, that the Cs pressure over $CsAlSi_5O_{12}$ is by a factor of 22 smaller than that over $CsAlSi_2O_6$. The compound $CsAlSiO_4$ has the largest vapor pressure exceeding that of $CsAlSi_2O_6$ by a factor of 56. Obviously, maximum retention of Cs can be obtained by the formation of $CsAlSi_5O_{12}$.

Besides the Cs partial pressures, the stability, and leachability of the Cs containing phase are further criteria for the final disposal of solidified liquid waste of high level radioactivity [17, 18]. Considering the stability, crystalline compounds are more suitable than glasses favoured in most countries. There are no data available to compare cesium containing glasses with cesium aluminosilicates regarding the leachability. The demand for crystalline compounds resulting from the stability criterion can be in contradiction to the demand for the minimum vapor pressure since the compound $CsAlSi_5O_{12}$ has a comparatively high SiO_2 content thereby favouring the formation of glasses during solidification. The formation of such a glassy phase is influenced by the solidification process [19]. Since until today there are no investigations considering the formation of glasses besides $CsAlSi_5O_{12}$ at different solidification processes it is impossible to decide whether $CsAlSi_5O_{12}$ is the most suitable phase to retain Cs during final storage.

Acknowledgements

The authors thank Professor Dr. H. W. Nürnberg, Director of the Institute of Applied Physical Chemistry, for the continuous kind support of these studies and valuable discussions. They are also indepted to Dr. H. Pentinghaus, Institute of Mineralogy, University of Münster, for his advice regarding the preparation and characterization of the various samples. The carrying-out of the X-ray investigations by the group of Dr. C. Freiburg, Central Unit of Chemical Analysis, KFA Jülich, is gratefully acknowledged. The skillful technical assistance of Mr. H. Gerads and his valuable ideas regarding the temperature measurement are particularly appreciated.

[1] R. Odoj and K. Hilpert, High Temp. — High Pressures, in press.

[2] A. K. Dé, B. Luckscheiter, W. Lutze, G. Malow, E. Schiewer, and S. Tymochowicz, Proc. of the Symposium on "Management of Radioactive Wastes from the Nuclear Fuel Cycle", Vienna, 1976, Vol. II, p. 63, IAEA SM-207.

[3] S. A. Gallagher, G. J. McCarthy, and D. E. Pfoertsch, Amer. Ceram. Soc. Bull. **55**, 461 (1976).

[4] K. Hilpert, R. Odoj, and H. W. Nürnberg, Proc. of the Reaktortagung 1977, p. 590, Mannheim, FRG, 1977; Zentralstelle für Atomkernenergie-Dokumentation (ZAED), Kernforschungszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen, FRG.

[5] R. M. Barrer, and N. McCallum, J. Chem. Soc. **821**, 4029 (1953).

[6] T. V. Solov'eva, G. A. Vydrik, and J. Kh. Moroz, Russ. J. Inorg. Chem. **15**, 909 (1970).

[7] R. Klaska, and O. Jarchow, Z. Kristallographie **142**, 225 (1975).

[8] G. Langlet, CEA-Report, France, CEA-R-3853, 1969.

[9] J. Ito, Amer. Mineral. **61**, 170 (1976).

[10] R. Odoj, Doctoral Thesis, University Bonn 1977; R. Odoj, K. Hilpert, and H. W. Nürnberg, KFA-Report, FRG, Jül-1460, 1977.

[11] K. Hilpert, and H. Gerads, High Temp. Sci. **7**, 11 (1975).

[12] K. Hilpert, Adv. in Mass Spectrometry, Vol. 7 A, p. 584, Heyden and Son Ltd., London 1978.

[13] K. Hilpert, Ber. Bunsenges. Phys. Chem. **83**, 161 (1979).

[14] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, Selected Values of the Thermodynamic Properties of the Elements, American Society of Metals, Metals Park, Ohio 1973.
[15] R. Odoj and H. Pentinghaus, in preparation.
[16] R. Odoj and K. Hilpert, in preparation.
[17] R. Roy, in: Scientific Basis for Nuclear Waste Management, Vol. 1, G. J. McCarthy ed., Plenum Press, New York 1979.
[18] W. Heimerl, H. Heine, L. Kahl, H. W. Levi, W. Lutze, G. Malow, E. Schiewer, and P. Schubert, HMI-Report, FRG, HMI-B 109, 1971.
[19] W. Heimerl, in: Scientific Basis for Nuclear Waste Management, Vol. 1, G. J. McCarthy ed., Plenum Press, New York 1979.