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TITLE THE FREE ENERGY OF FORMATION OF $\text{CaO} \cdot \text{SiO}_2$

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THE FREE ENERGY OF FORMATION OF CaCsCl_3 .

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ABSTRACT

The free energy of formation of the compound CaCsCl_3 from CaCl_2 and CsCl has been determined by measuring the sublimation pressure of CsCl(g) over $\text{CaCsCl}_3(\text{s})$ and over CsCl(s) using Knudsen effusion mass spectrometry. The free energy change for the reaction $\text{CaCl}_2(\text{s}) + \text{CsCl(s)} = \text{CaCsCl}_3(\text{s})$ at 298 K is $-40.7 \pm 6.4 \text{ kJ mol}^{-1}$. The enthalpy change is $-33.5 \pm 5.2 \text{ kJ mol}^{-1}$ and the entropy change is $23.4 \pm 3.7 \text{ J K}^{-1} \text{ mol}^{-1}$. Comparisons are made with determinations of these quantities by other investigators.

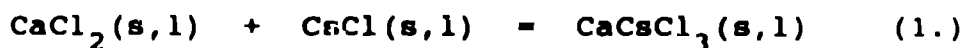
INDEX ENTRIES

CaCsCl_3 , free energy of formation, enthalpy of formation, entropy of formation, Knudsen effusion mass spectrometry.

INTRODUCTION

The free energy of formation of the ternary compound CaCsCl_3 is used in modeling the quaternary Ca-Cs-Pu-Cl in the 600 to 700 °C range. All of the results available are either on the liquid phase or give only the enthalpy of formation of the solid.

The free energy of mixing to form the liquid CaCsCl_3 from CsCl and CaCl_2 has been calculated from measured vapor pressures over the melt at 1373 and 1423 K by Topor and Moldoveanu(1.). The total pressure of $\text{CsCl}(g)$ and $\text{Cs}_2\text{Cl}_2(g)$ was measured. The free energy of mixing has also been determined by emf measurements on molten CaCsCl_3 at 1243 K by Emons and Brautigam(2.). The enthalpy of mixing for the reaction:



has been measured by Ostvold(3.) at 1136 and 1167 K. The measurements were made in the liquid region from mole fraction CaCl_2 0.0 to approximately 0.3 and from approximately 0.65 to 1.0. The fitted curve allows one to calculate the enthalpy of mixing at the composition $(\text{CaCl}_2)_{0.5}(\text{CsCl})_{0.5}$. The enthalpy of formation of the compound $\text{CaCsCl}_3(s)$ at 298 K has been measured by aqueous solution calorimetry by Sorokina, Smirnov, and Vasil'kova(4.). This same quantity has also been measured

at 728 K by Papatheodorou(5.) by solution calorimetry using the LiCl-KCl eutectic. The enthalpy of mixing has also been calculated from enthalpy measurements on CsCl(s,l), 0.12 CaCl₂(s,l)/0.88 CsCl(s,l), and CaCsCl₃(s,l) by Markov, Tishura, and Budarina(6.)

The free energy of formation of the compound CaCsCl₃(s) from CaCl₂ and CsCl ($\Delta_f G^\circ(\text{CaCsCl}_3, s, T) - \Delta_f G^\circ(\text{CaCl}_2, s, T) - \Delta_f G^\circ(\text{CsCl}, s, T)$) can be determined by measuring the sublimation pressure of CsCl(g) above the two phase region CaCsCl₃-CaCl₂. The phase diagram of the pseudo-binary (CaCl₂)-(CsCl) is shown in Figure 1(6.-10.). Over the temperature range 600-900 °C in which the 2 phase region is stable, the pressure of CsCl(g) is 4 orders of magnitude greater than that of CaCl₂(g) and can be measured with a Knudsen effusion mass spectrometer. The pressure, P(CsCl,g) is measured for the decomposition reaction:



The activity, a, which is by definition equal to the ratio, P(CsCl,g)/P⁰(CsCl,g), can be calculated from the sublimation pressure, P⁰(CsCl,g), for the reaction:



The free energy change of reaction 1 is equal to the free energy change for reaction 3 minus the change for reaction

The equation for the free energy change is:

$$\Delta G^{\circ}(T) = \Delta H^{\circ}(T) - T\Delta S^{\circ}(T) = -RT \ln(CIT/P^{\circ}) \quad (4.)$$

where I is the ion current due to CsCl(g) in reaction 2 and P° is the pressure of CsCl(g) in reaction 3. The calibration constant for the instrument is C.

METHODS

The sample of CsCaCl(s) was prepared by mixing finely divided powders of CsCl(s) and CaCl₂(s) and sealing them in a quartz ampoule under 1×10^5 Pa of argon. Ultra dry, 99.995% pure CaCl₂ (Aesar, Johnson Matthey Inc.) and 99.9995% pure CsCl (Aldrich) were used as the starting materials. All preparations were done in an argon-inerted glove box with approximately 1 ppm H₂O and 1 ppm O₂ as impurities in the glove box atmosphere. The starting materials were combined in a mole ratio corresponding to 55 mole % CaCl₂, mixed thoroughly, and reacted at 1075 °C for 0.5 hours. The product was then annealed at 675 °C for 100 hrs. The product was identified by Debye-Scherrer X-ray powder diffraction to be a mixture of CaCsCl₃(s) and CaCl₂(s) with most of the sample consisting of CaCsCl₃(s).

The sample was then placed in a platinum Knudsen effusion cell whose dimensions were 11 mm long by 6.35 mm in diameter. The diameter of the cell orifice was 0.79 mm and

the cell wall thickness was 0.4 mm. The sample itself was contained in a platinum cup 8 mm high by 5 mm in diameter with a wall thickness of 0.1 mm. The entire platinum cell was placed inside a molybdenum cell 21 mm high with an outside diameter of 12.7 mm. The lid of the molybdenum cell had a 3.2 mm hole in it. The cell temperature was measured with a chromel-alumel thermocouple. The rest of the apparatus is described in more detail in reference 11.

The sample of $\text{CaCsCl}_3(\text{s})$ was heated to a temperature of 500°C and the mass spectrum was scanned. Only the peak assigned to the ion Cs^+ was of appreciable intensity and was shutterable. The measured fragment ion appearance potential of 8.3 ± 1.0 eV (literature value 8.47 ± 0.07 eV(12.)) indicated this ion to be coming from the neutral precursor CsCl . The ion intensity of Cs^+/CsCl at 50 eV was measured over the temperature range 499 to 612°C .

A sample of $\text{CsCl}(\text{s})$ was sublimed in the same Knudsen effusion cell at a temperature of approximately 480°C to measure the sensitivity of the instrument. The mass spectrum was scanned and only the shutterable peak assigned to the ion Cs^+ was of appreciable intensity. The measured fragment ion appearance potential of 8.3 ± 1.0 eV indicated this ion to be coming from the neutral precursor $\text{CsCl}(\text{g})$ and had the same value as the ion Cs^+ did in the $\text{CaCsCl}_3(\text{s})$ sublimation. The Cs^+ intensity, I^0 , was measured at 50 eV.

DISCUSSION

For reaction 2 the measured values of $I(\text{Cs}^+)T$ as a function of $10^3 T^{-1}(\text{K})$ are given in Table 1 and are plotted in Figure 2. This curve was fit to the equation $\ln(IT) = AT^{-1} + B$. The calculated parameters were $A = -28,052. \pm 393.$ and $B = 17.928 \pm 0.482$. From this data the enthalpy change for the reaction 2 is $233.3 \pm 3.3 \text{ kJ mol}^{-1}$ and the entropy change is $147.5 \pm 4.0 + R \ln C \text{ J K}^{-1} \text{ mol}^{-1}$ at 829 K where C is the sensitivity of the instrument.

The measured values of $I^{\circ}(\text{Cs}^+)T$ for the sublimation of pure $\text{CsCl}(\text{s})$ according to reaction 3 are given in Table 2 as a function of $10^3 T^{-1}(\text{K})$. The calibration constant of the instrument is calculated from the values of $I^{\circ}T$ given in Table 2 and P° from the JANAF tables(13.). The values at the different temperatures were averaged to give $6.3 \pm 0.7 \times 10^{-4} \text{ bar amp}^{-1} \text{ K}^{-1}$.

A possible source of error in this measurement is contribution of the dimer, $(\text{CsCl})_2$, to the measured Cs^+ ion intensity at 50 eV. For the sublimation of CsCl the pressure ratio of dimer to monomer has been calculated to be 0.18 at 600 K and 0.53 at 900 K. For the sublimation of CaCsCl_3 , the contribution of the dimer to the total pressure and to the Cs^+ intensity at a given temperature will be smaller because the $\text{CsCl}(\text{g})$

pressure is reduced by approximately 10^{-3} and the dimer pressure reduced by 10^{-6} .

The results of Milne and Klein(14.) show that the $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratio is 0.10 at 950 K and 20 eV. The results of Berkowitz and Chupka(15.) give a ratio of 0.07 at approximately the same temperature and 70 eV. The Knudsen effusion mass spectrometry study of Milne and Klein(14.) obtained a second-law enthalpy of sublimation of $174.9 \pm 7.1 \text{ kJ mol}^{-1}$ for the Cs^+ ion and $200.8 \text{ kJ mol}^{-1}$ for the Cs_2^+Cl ion at 20 eV and 818 K. The second law slope for Cs^+ is close to the JANAF enthalpy value for reaction 3. On the basis of these observations it has been concluded that the major ionization process for CsCl(g) is $\text{CsCl} \rightarrow \text{Cs}^+ + \text{Cl}$ and for $(\text{CsCl})_2(\text{g})$ is $(\text{CsCl})_2 \rightarrow \text{Cs}_2\text{Cl}^+ + \text{Cl}$. The contribution to Cs^+ ion from $(\text{CsCl})_2$ at 50 eV is small and $(\text{CsCl})_2/\text{CsCl}$ pressure ratio is perhaps somewhat smaller than calculated from the JANAF tables(13.).

The terms $(H_T - H_{298})$ and $(S_T - S_{298})$ are found in the JANAF(13.) tables for CsCl(s,l) , CsCl(g) , and $\text{CaCl}_2(\text{s,l})$. The terms $(H_T - H_{298})$ and $(S_T - S_{298})$ for $\text{CaCsCl}_3(\text{s,l})$ are calculated from the results of Markov et al.(6.). More details are given in the appendix. The enthalpies and entropies of fusion and transition for CaCl_2 , CsCl , and CaCsCl_3 affect the shape of the curves $\Delta(H_T - H_{298})$, $\Delta(S_T - S_{298})$, and $\Delta(\text{FEF}_T - \text{FEF}_{298})$ for reaction 1. The four temperatures at which the curve has a discontinuity or changes slope are 743, 918, 1045, 1190 K.

The measured enthalpy and entropy changes of reaction 2 are given in Table 3 along with the corresponding changes for reaction 3 given in the JANAF tables(13.). The difference between the enthalpy changes for reactions 3 and 2 gives the change for reaction 1. The entropy change for reaction 1 is calculated the same way. The changes are given at 829 K and 298 K in the table. The free energy change for reaction 1 is calculated from the enthalpy and entropy changes.

The enthalpy change for reaction 1 obtained by other investigators is compared with the results of this study in Table 4. The enthalpies of reaction obtained by Sorokina et al.(4.), Papatheodorou(5.), Ostvold(3.), and Markov et al(6.) when corrected to 298 K agree with each other to within 2.2 kJ mol⁻¹ and are within 4.0 kJ mol⁻¹ of our value.

The entropy change of reaction 1 obtained in this work is compared with the entropy of mixing obtained indirectly by Topor and Moldoveanu(1.) and Emons and Brautigam(2.) in Table 5. The entropy of mixing or entropy change for reaction 1 can be calculated from the relation:

$$\Delta S^{\circ}(1, 298 \text{ K}) = -[\Delta G^{\circ}(1, T) - \Delta H^{\circ}(1, 298 \text{ K}) - \Delta(H^{\circ}_T - H^{\circ}_{298})]T^{-1} - \Delta(S^{\circ}_T - S^{\circ}_{298}). \quad (5.)$$

The value of $\Delta H^{\circ}(1, 298 \text{ K})$ is $-36.0 \pm 1.4 \text{ kJ mol}^{-1}$ from the average in Table 4 and the values of $\Delta G^{\circ}(1, T)$ are taken from Table 6. The entropy changes are given at temperature and at 298 K.

The values range from 12.4 to 23.4 J K⁻¹ mol⁻¹ at 298 K. The entropy change when calculated from the difference between the free energy and enthalpy is sensitive to small changes in these quantities. The entropy change is also sensitive to the second law slope for reaction 2.

The free energy change measure by Emons and Brautigam(2.) and by Topor and Moldoveanu(1.) are corrected to 298 K using $\Delta S^0(1,298\text{ K})$ given in Table 5. The free energy changes agree to within 1.3 kJ mol⁻¹. The average of the four determinations is -40.3 +/- 0.6 kJ mol⁻¹.

SUMMARY

By measuring the sublimation pressure of CsCl(g) over CaCsCl₃(s), we obtain an enthalpy change of -33.5 +/- 5.2 kJ mol⁻¹, an entropy change of 24.2 +/- 3.7 J K⁻¹ mol⁻¹ and a free energy change of -40.7 +/- 6.4 kJ mol⁻¹ at 298 K. The enthalpy values are within 4 kJ mol⁻¹ of the values of Sorokina et al(4.), Ostvold(3.), Papa-theodorou(5.) and Markov et al(6.). Our value for the free energy change agrees with the values of Topor and Moldoveanu(1.) and Emons(2.) to within +/- 1 kJ mol⁻¹. Our entropy change for reaction 1 differs by 11.0 J K⁻¹ mol⁻¹ with Topor and Moldoveanu(1.) and by 6.4 J K⁻¹ mol⁻¹ with Emons and Brautigam(2.). Based on results from the literature cited in this paper and this work the best fit to the data indicated that the enthalpy change for reaction 1 is -36.0 +/- 1.4 kJ mol⁻¹,

the free energy change is $-40.3 \pm 0.6 \text{ kJ K}^{-1} \text{ mol}^{-1}$, and the entropy change is $14.4 \pm 1.5 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K. The entropy change is calculated from the average values of ΔG and ΔH at 298 K.

APPENDIX

The thermodynamic functions $(H_T - H_{298})$ and $(S_T - S_{298})$ for $\text{CaCsCl}_3(\text{s}, \text{l})$ have been calculated by fitting the enthalpy data of Markov et al(6.) in the solid and liquid regions. For the solid, the function $(H_T - H_{298})$ was fit to $a + bT + cT^2$. The heat capacity derived from this is $C_p^0(T) = 99.54 (\pm 6.04) + 37.70 (\pm 3.81) \times 10^{-3} \times T \text{ (J K}^{-1} \text{ mol}^{-1})$. The heat capacity of the liquid was obtained by fitting the enthalpy values above the melting point to the function $a + bT$. The heat capacity derived from this is $C_p^0(T) = 191.54 (\pm 1.83) \text{ J K}^{-1} \text{ mol}^{-1}$. The enthalpy of melting was taken to be $80.49 \pm 0.4 \text{ kJ/mole}$ to fit the data of Markov et al(6.) and the melting point of 1190 K which we have selected from the data of Langenbach and Seifert(8.) The enthalpy values are $(H_{1000} - H_{298}) = 87.040 \text{ kJ mol}^{-1}$ and $(H_{1500} - H_{298}) = 253.659 \text{ kJ mol}^{-1}$. The entropy values are $(S_{1000} - S_{298}) = 145.925 \text{ J K}^{-1} \text{ mol}^{-1}$ and $(S_{1500} - S_{298}) = 283.382 \text{ J K}^{-1} \text{ mol}^{-1}$.

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TABLE 1. Measured Cs^+ ion intensity times temperature for the reaction $\text{CaCsCl}_3(\text{s}) = \text{CaCl}_2(\text{s}) + \text{CsCl}(\text{g})$.

No.	Seq.	T K	$10^3/T$ K^{-1}	IT amp K
1	7	885.2	1.1298	1.009×10^{-6}
2	6	874.0	1.1443	7.765×10^{-7}
3	8	868.8	1.1511	5.581
4	1	815.6	1.2263	6.379×10^{-8}
5	2	812.9	1.2303	5.780
6	11	810.2	1.2344	5.687
7	10	810.1	1.2346	5.752
8	9	809.0	1.2362	5.834
9	5	773.9	1.2923	1.032
10	4	772.8	1.2941	1.128
11	3	772.1	1.2943	1.043

$$\ln I^m = -28,052. (+/- 393.) T^{-1} + 17.928 (+/- 0.482)$$

$$T_{\text{med.}} = 829. \text{ K}$$

TABLE 2. Measured Cs^+ ion intensity times temperature for the reaction $\text{CsCl(s)} = \text{CsCl(g)}$.

No.	Seq.	T K	$10^3/T$ K^{-1}	$I^{\circ}T$ amp K	$C \times 10^2$ bar $\text{amp}^{-1}\text{K}^{-1}$
1	4	763.3	1.3103	1.121×10^{-5}	7.12
2	3	760.0	1.3159	1.237	5.67
3	2	759.6	1.3165	1.204	5.74
4	1	742.7	1.3466	5.231×10^{-6}	6.62
					avg. 6.29 +/- 0.70

TABLE 3. Enthalpy, entropy and free energy changes for reactions 1, 2, and 3 at 829 K and 298 K.

Function	Reaction	$\Delta Y(829 \text{ K})$	$\Delta Y(298 \text{ K})$
ΔH	3	187.9 +/- 4.3	202.7 +/- 4.3
	2	233.2 +/- 3.0	236.2 +/- 3.0
	1	-45.4 +/- 5.2	-33.5 +/- 5.2
ΔS	3	129.6 +/- 0.03	154.9 +/- 0.03
	2	126.1 +/- 3.7	131.5 +/- 3.7
	1	3.5 +/- 3.7	23.4 +/- 3.7
ΔG	1	-48.3 +/- 6.7	-40.5 +/- 6.7

TABLE 4. Comparison of different determinations of the enthalpy change for the reaction for $\text{CaCl}_2(\text{s}) + \text{CsCl}(\text{s}) = \text{CaCsCl}_3(\text{s})$ at 298 K.

Investigator	T K	$\Delta H^\circ(T)$ kJ mol ⁻¹	$\Delta H^\circ(298 \text{ K})$ kJ mol ⁻¹
Sorokina-72(4.)	298.	-36.4 +/- 0.4	-36.4 +/- 0.4
Papatheodorou-74(5.)	728.	-41.9 +/- 0.8	-35.3 +/- 0.8
This work	829.	-45.4 +/- 5.2	-33.5 +/- 4.6
Ostvold-72(3.)	1136.	-24.48 +/- 0.33	-37.50 +/- 0.33
Ostvold-72(3.)	1167.	-23.51 +/- 0.42	-36.92 +/- 0.42
Markov-74(6.)	1213.	-21.8 +/- 0.8	-36.1 +/- 0.8
			avg. -36.0 +/- 1.4

TABLE 5. Comparison of different determinations of the entropy change for the reaction $\text{CaCl}_2(\text{s}) + \text{CsCl}(\text{s}) = \text{CaCsCl}_3(\text{s})$ at 298 K.

Investigator	T K	$\Delta S^\circ(T)$ $\text{J K}^{-1} \text{mol}^{-1}$	$\Delta S^\circ(298 \text{ K})$ $\text{J K}^{-1} \text{mol}^{-1}$
This work	829.	3.5 +/- 3.7	23.4 +/- 3.7
Emons-76(2.)	1243.	9.9	17.0
Topor-78(1.)	1373.	7.5	13.3
Topor-78(1.)	1423.	7.0	12.4
		avg.	16.5 +/- 5.0

TABLE 6. Comparison of different determinations of the free energy change for the reaction $\text{CaCl}_2(\text{s}) + \text{CsCl}(\text{s}) = \text{CaCsCl}_3(\text{s})$ at 298 K.

Investigator	T K	$\Delta G^\circ(T)$ kJ/mole	$\Delta G^\circ(298 \text{ K})$ kJ/mole
This work	829.	-48.3 +/- 6.4	-40.7 +/- 6.4
Emons-76(2.)	1243.	-33.6	-41.0
Topor-78(1.)	1373.	-30.1	-39.9
Topor-78(1.)	1423.	-29.2	-39.7
			avg. -40.3 +/- 0.6

FIGURES

FIGURE 1. Phase diagram for the psuedo-binary system $(\text{CaCl}_2)-(\text{CsCl})$. Diagram is based on the calculations of Murray(10.) and the data of; Burlakova and Bukhalova(7.), Markov, Tishura and Budarina(6.), Seifert and Langenbach(8.), and Shakno and Plyushchev(9.).

FIGURE 2. Ion intensity of Cs^+ times temperature for the reaction $\text{CaCsCl}_3(\text{s}) = \text{CaCl}_2(\text{s}) + \text{CsCl}(\text{g})$ as a function of inverse temperature.

