



VARIABLE COMPOSITION OF CHLORINE HYDRATES SYNTHESIZED UNDER VARIOUS CONDITIONS

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Keywords: Chlorine hydrate, clathrate cage; occupancy, density

The composition of chlorine hydrates synthesised by different reaction routes were determined from experimentally measured density values without isolating the gas hydrate crystals. This method is the simplest and accurate for determining the composition of chlorine hydrates prepared under various conditions. The occupancies of each type of the cavities in the clathrate cage have been calculated.

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Introduction

Chlorine hydrate is the first gas hydrate discovered by Davy.¹ It is widely used as solid chlorine source in various important products and technological processes such as high energy density batteries, refrigerators, disinfection processes and high pressure chlorination reactions.² The determination of the composition of chlorine hydrate has attracted attention of chemists for long time because of its non-stoichiometric nature and dependence of its composition on the conditions of the preparatory methods.²⁻¹¹ The use of various oxidants as starting materials for the oxidation of hydrochloric acid e.g. hypochlorites or possible new oxidants such as simple or complex permanganates give new perspectives in the preparation of this compound.^{2,11-15} Besides, the composition of the crystals formed depends on the conditions of the methods used for its preparation, a simple and easy method to determine the composition of chlorine hydrate formed without isolation of crystals is required because instability of the crystals during weighing is the main problem in the analysis of the chlorine hydrate.^{9,10}

Results and Discussion

Chlorine hydrate belongs to the type I clathrate hydrates that consist of a 46 membered 3D-network of water molecules including 2 small and 6 large voids. The formula of chlorine hydrate can be written as $(8-x)\text{Cl}_2 \cdot 46\text{H}_2\text{O}$, where x is the number of the unfilled voids in the elementary cell ($Z=1$).³ This formula can also be expressed as $\text{Cl}_2 \cdot n\text{H}_2\text{O}$,

where n is the number of water molecules, termed as hosts, that encage one molecule of the chlorine gas termed as the guest. It theoretically means that the chlorine hydrate, which is richest in chlorine, could be characterized with the formula derived from the maximal filling ratio, namely $\text{Cl}_2 \cdot 5.75\text{H}_2\text{O}$. Since the density can easily be determined experimentally with high accuracy without separating the crystals from the mother liquor^{16,17}, these density values can therefore be used for calculation of the composition of the chlorine hydrates. The general formula of the chlorine hydrate can also be written as $(6\theta_1\text{Cl}_2 + 2\theta_2\text{Cl}_2) \cdot 46\text{H}_2\text{O}$, where θ_1 and θ_2 are the occupancies of the larger and smaller cavities respectively. The density can be expressed as the quotient of the molar mass and the molar volume of each clathrate. The molar mass of the hydrate can be calculated as the sum of the weights of the guest and the water cage, and the molar volume can be expressed by using the known temperature dependent molar volume of the blocks of 46 water molecules of the ice lattice by using the additional term $\Delta V(T, n)$ ¹⁸:

$$V_{\text{clathrate}}^T = V_{\text{ice}}^T + \Delta V(T, n) \quad (1)$$

where T is the absolute temperature in K, and n means the occupancy. The $\Delta V(T, n)$ term can be divided into two parts,

$$\Delta V(T, n) = \Delta V_{n=0} + \Delta V_a(T, n) \quad (2)$$

where $\Delta V_{n=0}$ value is constant and can be taken as 3.0^3 or $3.2 \text{ cm}^3/\text{mol}$ ¹⁹. The value of the additional term, $\Delta V_a(T, n)$ depends on the number of chlorine molecules and includes the effect of the thermal motion on the strength of the host-guest interactions in each type of the cavities^{20,21}. The contribution of the $\Delta V_a(T, n)$ term on the $\Delta V(T, n)$ values, however, proved to be not substantial because the widening of the clathrate hydrate cage reaches roughly 1 % value at the $D_M = 5.7 \text{ \AA}$ ²² diameter of the guest molecule, and the D_{Cl_2} is only 5.2 \AA ³. The calculated n_1 values were compared with the n_2 values determined from the known lattice constant 3 and experimental density values (Eqn.(3) and (4)),^{17,18}

$$d_{\text{exp}} = \frac{[(6\theta_1 M_X + 2\theta_2 M_X) + 46M_{H_2O}]}{N_A a^3} \quad (3)$$

where M_{H_2O} is the molar mass of the water, $N_A = 6.0238$, the Avogadro number, and θ_1 and θ_2 are the occupancies.

$$n_1 = \frac{46}{6\theta_1 + 2\theta_2} \quad (4)$$

The use of $\Delta V_{n=0} = 3.1 \text{ cm}^3/\text{mol}$, average value in our calculations, resulted in n_1 and n_2 values that are given in Table 1 for various chlorine hydrates prepared under different conditions. The calculated n_1 and n_2 values are very close to each other. The kinetic factors have great importance because any two samples prepared in the same way but from different charges usually do not provide the same composition before attaining the complete equilibrium state.^{7,10,11} Faraday found that the density of the plate like chlorine hydrate crystals was $d = 1.2$ by a flotation density measurement method.⁶ Since there was continuous gas liberation and the imperceptible bubbles might have adhered to the hydrate surface, therefore the density could be presumed to be less than $d = 1.2 \text{ g/cm}^3$. Thus the composition can be formulated as $\text{Cl}_2 \cdot 7.63\text{H}_2\text{O}$. Roozeboom experimentally determined the density of two samples of crystalline chlorine hydrate to be $d = 1.220$ and 1.237 g/cm^3 .⁹ These values correspond to the $\text{Cl}_2 \cdot 7.28\text{H}_2\text{O}$ and $\text{Cl}_2 \cdot 7.00\text{H}_2\text{O}$ formulas, respectively. This indicated that the water content might have been less than what Roozeboom had observed by direct chemical analysis.⁹ The chlorine hydrate prepared in zinc chloride solutions can be compacted and stabilized with pressure. If the pressure is below 60 atm, the density falls below 1 g/cm^3 , but at 70-80 atm. pressure the value increases to $1.1-1.2 \text{ g/cm}^3$ and becomes 1.23 g/cm^3 above 800 atm. Further increase in the pressure does not result in significant increase in the density value.²³

Table 1. Experimental densities, lattice constants and composition values of the chlorine hydrates at 273.15 K.³

Reference	d, g/cm ³	n_1	n_2	θ_1	θ_2
Faraday ⁶	1.2	7.63	7.58	1.00	0.03
Roozeboom ⁹	1.220	7.28	7.23	1.00	0.17
	1.237	7.00	6.95	1.00	0.32
Bjorkman ²³	1.23	7.11	7.07	1.00	0.25
Wilms ⁵	1.239	6.97	6.92	1.00	0.37
Smirnov ²⁵	1.31	6.01	5.98	1.00	0.85
Kislovskii ²⁴	1.37	-	-	-	-

*Density of two samples prepared in different ways were determined

Smirnov and Kleshchunov reported an experimentally determined value of density (1.31 g/cm^3) for the isolated chlorine hydrate which was found to have the formula $\text{Cl}_2 \cdot 6.2\text{H}_2\text{O}$.²⁵ The use of this density value provided the composition of the hydrate to be $\text{Cl}_2 \cdot 6.01\text{H}_2\text{O}$, which is close to the experimentally found value ($n_3=6.2$).²⁵

A density value of 1.37 g/cm^3 was given for a chlorine hydrate formed in capillaries. This value is too large even if a complete occupation ($8\text{Cl}_2 \cdot 46\text{H}_2\text{O}$) is supposed ($d = 1.325 \text{ g/cm}^3$), thus the lattice of the chlorine hydrate should be contracted in the capillaries ($a = 1.192 \text{ \AA}$) or the difference between the molar volumes of the empty clathrate cage and the ice should be diminished from the average 3.1 to $2.5 \text{ cm}^3/\text{mol}$.² No example for this magnitude of contraction among the clathrate hydrates of gases, even at higher pressures than the observed 10-12 atm could be present in the capillaries and the perfect filling of the cavities should cause dilatation rather than contraction. Therefore, the hydrate formed in the capillaries probably does not belong to the clathrate type I but a different type of chlorine hydrate richer in chlorine is rather formed as mentioned by Maumene, and a rhombic polymorph of the chlorine hydrate was also detected by Nordenskjöld.^{2,26,27}

Conclusions

The composition of chlorine hydrates prepared by different reaction routes were determined based on their experimentally measured density values. This method is the simplest and accurate way for the determination of the composition of chlorine hydrates prepared under various conditions because it does not require isolation of the crystals from the solution. The composition of various chlorine hydrates prepared in the last 200 years was re-determined and the values were found between 6.01 and $7.63\text{H}_2\text{O}/\text{chlorine}$ molecule. The results found for the chlorine hydrate prepared in capillaries ($d=1.37 \text{ g/cm}^3$) showed that this chlorine hydrate cannot be type I clathrate hydrate but a new modification or an other type of the chlorine hydrate might be formed within the capillaries.

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Received: 23. April 2012.

Accepted and published online: 31. May 2012