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The Minimal Occupancy Level of the Clathrate Hydrate Host Lattice and the Intercalation Heat of the Guest Molecules in the Chlorine Hydrates

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Keywords: Clathrate hydrates; Clathrates; Chlorine; Intercalation heat; Minimal occupancy level

Abstract. The minimal occupancy level (θ_{\min}) of the clathrate lattice of gas molecules is defined as the number of guest molecules in the host clathrate lattice, which can stabilize the thermodynamically unstable empty cage by covering the energy demand of the transforma-

tion of hexagonal ice into empty clathrate lattice (ΔH_{trans}). The θ_{\min} values for chlorine hydrate were determined from the $n = f(p)_{T=\text{const.}}$ relationship and the average molar intercalation heat of chlorine in the type I clathrate lattice was also calculated for both type of cavities.

Introduction

Clathrate hydrates of gases like methane or chlorine are important as solid energy sources or electrodes of high energy density batteries.^[1,2] The determination of the composition and thermodynamic properties of these clathrate type gas hydrates have attracted attention for long time, because of their non-stoichiometric nature and dependence of their composition on the conditions and the method of preparation.^[2–8] The type I gas hydrates can be characterized with the $(8-x)M \cdot 46\text{H}_2\text{O}$ formula, where x means the number of the unfilled cages in the elementary cell of the hydrate ($Z = 1$), or it can also be described as $M \cdot (5.75+y)\text{H}_2\text{O}$, where $y+5.75 = n$ and n is the number of water molecules per gas called as guest. It theoretically means that the hydrate, which is the richest in hydrate forming gas could be characterized by the formula derived from the maximal filling ratio.^[8] The lowest occupation level, θ_{\min} , where the hydrate is just stable (the empty hydrate cage is thermodynamically unstable), however, has not been known. Since the van der Waals interaction energies between various

guest molecules and water cage are different, consequently the minimal occupancy level and the molar intercalation energies of each gas should be different.

Results and Discussion

The minimal occupancy level of the type I clathrate hydrate host cage by guest molecules is defined as the number of the guest molecules in the 46-membered elementary unit. Since the intercalation heat of these guest molecules have to cover the energy demand of the formation of the empty clathrate cage from the hexagonal ice, the sum of the intercalation heats of the guests at the minimal occupancy level will be equal to the energy difference between the empty clathrate cage and the hexagonal ice. It is obvious, that the intercalation heat in the larger and smaller cavities within the clathrate cage are not equal, and the intercalation heat could be dependent on the filling as well, but in first approximation, we take into consideration average intercalation heats (ΔH_1^i and ΔH_2^i), where index 1 and 2 refer to the large and small cavities in the clathrate cage, respectively.

$$6\alpha_1^{\min}\Delta H_1^i + 2\alpha_2^{\min}\Delta H_2^i = \Delta(\Delta H_{\text{ice}} - \Delta H_{\text{clathrate}}^e) \quad (1)$$

In Equation (1) α_1 and α_2 refer to the six large and two small cavities, respectively. The ΔH_{ice} means the heat of formation of ice and $\Delta H_{\text{clathrate}}^e$ means the heat of formation of empty clathrate cage. The energy difference between the hexagonal ice and cubic empty clathrate lattice is known, its value is given as $\Delta H_{\text{trans}} = 275$ and $269 \text{ cal} \cdot \text{mol}^{-1} \text{ H}_2\text{O}$,^[9] respectively. In order to determine the molar intercalation heat, however, the minimal occupation level has to be determined. As one of the most important gas hydrate,^[2] chlorine hydrate was selected to represent its determination method.

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The composition of the chlorine hydrate formed from water vapor and chlorine gas with various stoichiometries were prepared at defined temperature and pressure conditions.^[6] By selecting the $p = f(n)_{T=\text{const.}}$ isotherms, the curves converge to a given n value where the minimal occupancy is observed. There is no physical meaning of the functions below this n values, because the chlorine hydrate does not exist above this n values. Since this n level depends on the temperature, a confidence interval ($\Delta n = 0.01$) was taken, thus instead of the intersection of the curves we could define a p, n pair value, where the confidence intervals of each curves are contacted and the values ($n = 9.50$ and $p = 0.06$ atm) obtained by this point were taken as the point of the minimal occupancy (θ_{\min}) (Figure 1). Taking into consideration the temperature dependence and neglecting the confidence interval, the three curves would converge to three different (although very close) n values and would never meet.

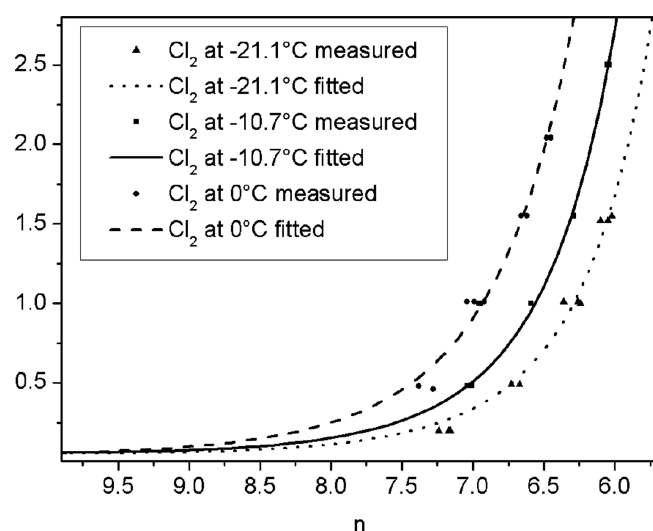


Figure 1. Composition-dissociation pressure isotherms of chlorine hydrates.

The value of $n = 9.5$ defines the formula of the chlorine hydrate which contains the minimal amount of chlorine in the cages to stabilize the clathrate lattice as $4.84\text{Cl}_2 \cdot 46\text{H}_2\text{O}$. By assuming that all of the 4.84 chlorine molecule are located in the large cavities,^[5] the $\alpha_1^{\min}(\text{Cl}_2)$ value is 0.8067, and the $\alpha_2^{\min}(\text{Cl}_2)$ value is 0. By starting from the average value of the $\Delta H_{\text{trans}} = 272 \text{ cal} \cdot \text{mol}^{-1} \text{ H}_2\text{O}$, the energy difference between 46 molecules of hexagonal ice and a 46-membered empty clathrate cage is:

$$\Delta(\Delta H_{\text{ice}} - \Delta H_{\text{clathrate}}) = 46\Delta H_{\text{trans}} \quad (2)$$

By substituting the result and the two α_{\min} values into Equation (2), the average intercalation heat of the chlorine molecule in the large cavities of type I clathrate cage is found to be $\Delta H_1^i = 2.585 \text{ kcal} \cdot \text{mol}^{-1} \text{ Cl}_2$ gas.

Von Stackelberg determined the pycnometric density, ($d = 1.29 \text{ g} \cdot \text{cm}^{-3}$), the lattice constant (1.203 \AA) and the composi-

tion ($n = 5.9 \pm 0.3$) of the chlorine hydrate.^[8] Based on the density and lattice constant values, the real composition of the given hydrate was $n = 6.22$,^[2] thus the α_1 and α_2 values for this chlorine hydrate are 1.0 and 0.695. Substituting the known average ΔH_1^i value into Equation (1), the average ΔH_2^i value can be determined ($\Delta H_2^i = 2.951 \text{ kcal} \cdot \text{mol}^{-1} \text{ Cl}_2$). The $\Delta H_1^i < \Delta H_2^i$ relationship unambiguously shows, that the interaction energy of the chlorine with the water molecules are higher in the smaller cavities due to the closeness of these water molecules to the guest chlorine molecule.

Having the knowledge of average ΔH_1^i and ΔH_2^i values, the heat of formation of various chlorine hydrates prepared with various n values can be estimated. The results of this calculation for the chlorine hydrate formed from gaseous components and from chlorine gas and liquid water is given in Table 1 and Table 2, respectively. The ΔH^f values for reactions involving water in different state (solid, liquid, or vapor) were determined by using melting and evaporating enthalpy values of water.^[3,8]

Table 1. Calculated heat of formation $/\text{kcal} \cdot \text{mol}^{-1}$ of various chlorine hydrates in the $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{Cl}_2 \cdot n\text{H}_2\text{O}(\text{s})$.

n	$\alpha_2^{\text{a)}}$	ΔH^f	T / K	p / atm
6.02	0.821	81.24	252.05	1.55
6.24	0.685	83.13	252.05	1.00
7.19	0.199	91.86	252.05	0.20
6.05	0.802	81.49	262.45	2.50
6.29	0.657	83.57	262.45	0.48
7.03	0.272	90.34	262.45	0.48
6.47	0.555	85.17	273.15	2.04
6.96	0.305	89.68	273.15	2.04
7.28	0.159	92.73	273.15	0.46

a) $\alpha_1 = 1$ (complete occupation). b) The used experimental composition values were taken from reference^[6].

By calculating with this method, the ΔH^f values at complete filling of the cavities with chlorine would be $8.76 \text{ kcal} \cdot \text{mol}^{-1}$, $17.03 \text{ kcal} \cdot \text{mol}^{-1}$ and $79.00 \text{ kcal} \cdot \text{mol}^{-1}$ from ice, liquid water or water vapor, respectively. By comparing the available heat of formation values for the chlorine hydrate formed from ice or liquid water and chlorine, the values found by this method are close enough to each other.^[2,3] The most reliable heat of formation value calculated for chlorine hydrate from the dissociation tension curve was provided by von Stackelberg as $\Delta H^f = 15.5 \pm 0.5 \text{ kcal} \cdot \text{mol}^{-1}$ and ΔH^f value found by calorimetry was $16.9 \pm 0.5 \text{ kcal} \cdot \text{mol}^{-1}$.^[8] These values relate to the chlorine hydrate with the formula of $\text{Cl}_2 \cdot 6.2\text{H}_2\text{O}$,^[2,8] and the found $\Delta H^f = 15.96 \text{ kcal} \cdot \text{mol}^{-1}$ (see Table 2) value is located between these two experimental values.

Conclusions

This method can generally be used for the determination of the θ_{\min} and ΔH^i values not only for chlorine but for various gases forming clathrate type I gas hydrates.

Table 2. Calculated heat of formation /kcal·mol⁻¹ of various chlorine hydrates in the Cl₂(g)+H₂O(l) = Cl₂·nH₂O(s)^{a)}.

<i>n</i>	<i>α</i> ₁	<i>α</i> ₂	Δ <i>H</i> ^f	<i>T</i> /K	References ^{b)}
9.17	0.836	0	13.14	274.15	[5]
8.42	0.911	0	13.38	268.65	[5]
7.55	1.000	0.046	13.99	273.15	[5]
7.27	1.000	0.164	14.28	273.15	[10]
6.90	1.000	0.333	14.74	277.60	[7]
6.35	1.000	0.622	15.66	273.15	[11]
6.20	1.000	0.710	15.96	273.15	[8]
5.97	1.000	0.853	16.47	273.15	[11]

a) *p* = 1 atm. b) References for experimental composition values.

References

- [1] E. D. Sloan Jr., *Nature* **2003**, 426, 353; Y. F. Makogon, S. A. Holditch, T. Y. Makogon, *J. Petr. Sci. Eng.* **2007**, 56, 14; C. M. Blevins, *J. Power Sources* **1981–82**, 7, 121; S. Mitra, *J. Power Sources* **1982**, 8, 359.
- [2] L. Kótai, I. Gács, S. Bálint, Gy. Lakatos, R. N. Mehrotra, *Trends in Inorganic Chemistry*, **2011**, in press.
- [3] L. Kótai, F. Bódi, A. Sebestyén, S. Harfouch, *Hung. J. Ind. Chem.* **1991**, 19, 63.
- [4] L. Kótai, A. Nagy, F. Bódi, A. Sebestyén, *Hung. J. Ind. Chem.* **1999**, 27, 25–26.
- [5] L. Kótai, A. Nagy, F. Bódi, A. Sebestyén, *Hung. J. Ind. Chem.* **1999**, 27, 27.
- [6] G. H. Cady, *J. Phys. Chem.* **1981**, 85, 3225; G. H. Cady, *J. Phys. Chem.* **1983**, 87, 4437.
- [7] D. A. Wilms, A. A. Van Haute, *Desalination* **1973**, 12, 379.
- [8] M. von Stackelberg, *Naturwissenschaften* **1949**, 36, 327; M. von Stackelberg, *Naturwissenschaften* **1949**, 36, 359.
- [9] R. M. Barrer, W. I. Stuart, *Proc. Roy. Soc. London* **1958**, 243A, 172.
- [10] K. W. Allen, *J. Chem. Soc.* **1959**, 4131.
- [11] A. Bouzat, L. Azinieres, *Bull. Soc. Chim. Fr.* **1924**, 35, 545.

Received: August 31, 2011

Published Online: October 20, 2011