Simulation of structure and thermodynamic properties of the double of ozone and carbon dioxide hydrates using molecular and lattice dynamics methods

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Abstract. Ozone is a very effective medical, industrial and agricultural disinfecter, bleacher and deodorizer. Ozone acts very quickly, but its decay rate is also high. Gas hydrate formation is a promising method for storing ozone and ozone-containing gas mixtures. We use molecular dynamics (conjugate gradient) and lattice dynamics method to calculate the free energy double O\textsubscript{3}+CO\textsubscript{2} hydrate of cubic structure I at 270 K and 275 K temperatures and various gas phase compositions. It allowed determining the chemical potential of water molecules depending on pressure at given temperatures and compositions. Comparison with I\textsubscript{h} ice and liquid water allowed us to determine regions of O\textsubscript{3}+CO\textsubscript{2} double hydrate stability. The presented results may be useful in studies of thermodynamic stability areas of hydrates obtained from pure ozone (e.g. liquid ozone), its mixtures and in the development of corresponding storage technologies.

1. Introduction

Ozone's wide applicability in medicine, industry, agriculture and aquaculture is due to its very high oxidation potential and environmental friendliness when used in liquid form especially in rocket engineering as a replacement of O\textsubscript{2}. However ozone's oxidation is provided by the molecular breakdown and accompanied by the formation of toxic free radicals. There is no effective method for long-term storage of ozone. Along with dissolution in water and its subsequent freezing, ozone hydrate, the inclusion compound formed by water carcass, was obtained. Mean radius of hydrate cavities is about half a nanometer for various types of hydrate structure. The location of single ozone molecule in cavity does not allow its fast decaying. In order to design the technology of long-term storage of ozone at an acceptable temperature and pressure, a series of experimental works was carried out in order to find the helper gas, the hydrate structure of which would be more stable under the same conditions and accommodate a larger volume of ozone. Carbon tetrachloride, oxygen, xenon and carbon dioxide were used as helper gases for double and triple mixtures with ozone, however ozone mass fraction was experimentally found to be less than 1%. More detailed information may be found in the works [1,2].

One of the highest mass fractions of ozone was obtained by the authors of experimental work [3]: 2.15 mass\% in the O\textsubscript{3}+O\textsubscript{2}+CO\textsubscript{2} mixture at a temperature of 272 K and pressure of 3.0 MPa. Authors of [4] concluded that only hydrate formation could increase the mass fraction of stored ozone above 1% in comparison to ozonated ice and ozonated water. The search for the set of helper gases that will provide the optimal thermobaric conditions of gas mixed hydrate formation and the mass fraction of ozone in the hydrate is still ongoing.
Due to ozone fast decay its pure hydrate was not obtained. However the ozone half-life time greatly rises with temperature decrease that makes liquid ozone a promising substance for hydrate formation. Hypothetically, hydrate formation from liquefied ozone could increase the O3 mass fraction up to ~30% (every cavity is occupied by single O3 molecule). Despite the great importance of ozone hydrates there are not enough experimental works on this theme, so we selected ozone and ozone-based hydrates as the main subject of this paper.

In this paper we present the combined molecular dynamics (MD) and lattice dynamics (LD) method study of double O3+CO2 hydrate of cubic structure I (CS-I). This method allows obtaining optimized and stable hydrate structures in the wide range of temperatures and pressures, and calculating the corresponding Helmholtz free energy and chemical potential to determine the hydrate areas of stability. The main aim of this work is to find out the pressure of pure O3 and O3+CO2 double hydrates stability at 270 K and 275 K depending of gas phase composition.

2. Methods and simulation details

In this work, we study the CS-I gas hydrate (46 water molecules, 2 small and 6 large cages) and hexagonal structure crystalline ice Ih (128 water molecules) models.

The used combined approach consists of MD and LD methods. MD method is realized in the form of conjugate gradient method that excludes the thermal contribution and is used to obtain optimized hydrate structures. In other words, it is used to find potential energy minimum of every molecule at various set of model volumes that provides the data on system potential energies.

The LD method was used in order to simulate the molecule dynamic properties of considered double hydrates, e.g. the phonon spectrum. Calculation of eigen frequencies / zero-point oscillations was carried out for temperatures of 270 K and 275 K for the entire set of CS-I structure volumes. It allowed calculating Helmholtz free energy as a sum of potential energy and vibrational energy and determining the pressure in the structure of certain volume by calculating the volume derivative of Helmholtz free energy. Then the chemical potentials of water molecules and guest molecules were calculated. Details of this approach may be found in our previous works [5,6]. Varying the gas phase composition and comparing the corresponding chemical potentials allows determining the optimal gas phase composition and formation pressure at 270 K and 275 K. Detailed description of liquid water chemical potential calculation may be found in [7].

Both methods used modified [1] SPC/E [8] water potential with following Lennard–Jones potential parameters: \( \sigma = 3.1556 \) Å, \( \varepsilon = 0.65063 \) kJ/mol, and charges on hydrogen and oxygen atoms are \( q_H = +0.4238 |e| \) and \( q_O = -0.8476 |e| \), respectively. Guest molecule Lennard–Jones potential was used with the parameters \( \sigma = 3.875 \) Å and \( \varepsilon = 1.733 \) kJ/mol for ozone molecules [9], and \( \sigma = 4.00 \) Å and \( \varepsilon = 1.5798 \) kJ/mol for carbon dioxide molecules [10].

3. Results and discussion

Using the described method the dependence of water molecule chemical potential on pressure at 270 K and 275 K was calculated for hydrate structures with different gas mixture composition. Fig. 1 shows the corresponding dependencies for the cases when the fraction of ozone in the O3+CO2 gas mixture is 0%, 10%, 20%, 30%, 40% and 100%. At \( T = 270 \) K, comparisons are made with the chemical potential of water molecules for crystalline ice Ih. At \( T = 275 \) K, in addition a comparison with the chemical potential for water molecules in the liquid phase is made. Chemical potential equality allows determining the equilibrium conditions. The lower is the chemical potential of the structure, the more stable the structure is. Therefore, determining the existence conditions for the ozone-containing gas mixture hydrate at a temperature of 275 K required the comparison of chemical potential with that for water in the liquid phase.

From fig. 1 it is clearly seen that the pure ozone hydrate is more stable than gas mixture hydrates under pressure that are higher than 0.258 MPa at 270 K and ~0.634 MPa at 275 K. It can be seen that an increase of carbon dioxide fraction leads to an increase in the hydrate formation pressure, while the hydrate of pure carbon dioxide (100% mole fraction) has the highest hydrate formation pressure:
approximately 0.64 MPa at 270 K and 1.16 MPa at 275 K that well coincides with the known experimental data [11]: \( P = \sim 1 \) MPa at \( T = 270.7 \) K and \( P = 1.6 \) MPa at \( T = 275 \) K. Authors of [12] showed that at 97.4% \( \text{CO}_2 \) and 272.2 K mole fraction the formation pressure of \( \text{O}_3+\text{O}_2+\text{CO}_2 \) hydrate is 1.149 MPa.

![Figure 1](image)

**Figure 1.** The dependence of chemical potential of water molecules of the binary \( \text{O}_3+\text{CO}_2 \) hydrates of ozone and carbon dioxide, \( \text{Ih ice} \) and water on pressure at \( T = 270 \) K and \( T = 275 \) K for different ozone mole fraction in the gas phase: 0 % (squares), 10 % (circles), 20 % (triangles), 30 % (inverted triangles), 40 % (rhombus), and 100 % (left inverted triangles).

Table 1 summarizes the data on equilibrium pressure of “gas phase – ice phase – hydrate phase” at 270 K and “gas phase – water phase – hydrate phase” and 275 K for different compositions of the gas phase (fraction of ozone in \( \text{O}_3+\text{CO}_2 \) gas mixture).

| \( P^{270} \), MPa | \( x^{270} \), % | \( P^{275} \), MPa | \( x^{275} \), % |
|-------------------|----------------|----------------|----------------|
| 0.627             | 0              | 1.151          | 0              |
| 0.528             | 10             | 1.041          | 10             |
| 0.477             | 20             | 0.972          | 20             |
| 0.436             | 30             | 0.908          | 30             |
| 0.399             | 40             | 0.856          | 40             |
| 0.258             | 100            | 0.634          | 100            |

**Table 1.** Equilibrium pressure (\( P \)) and \( \text{O}_3 \) mole fraction (\( x \)) of “gas phase – ice phase/water phase – hydrate phase” systems for the \( \text{CO}_2+\text{O}_3 \) gas mixture at \( T = 270 \) K and \( T = 275 \) K.

**Conclusion**

For the first time the dependence of double \( \text{CO}_2+\text{O}_3 \) hydrate formation pressure on the fraction of ozone in gas phase has been demonstrated. \( P-x \) equilibria of gas phase–ice phase (liquid phase)–hydrate phase systems for the \( \text{CO}_2+\text{O}_3 \) gas mixture at \( T = 270 \) K and \( T = 275 \) K have been calculated. The addition of ozone is shown to reduce the pressure of CS-I mixed hydrate formation. The lowest pressure value reaches for pure \( \text{O}_3 \) case. Presented results have predictive nature because used method do not utilize any fitting parameter.
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