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Adsorption isotherm of the N_2–CO equimolar mixture in clathrate at 50K – Implications for the composition of solid bodies of the outer Solar System

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Abstract

Adsorption isotherms of CO, N_2 and their equimolar mixture are presented in the case of structure I clathrate. They have been computed via Monte-Carlo simulations in the Gibbs ensemble for fugacities at 50K and in the 10^{-11}–4.10^{-3} Pa pressure range, corresponding to the typical thermodynamic conditions at which clathrates form in the protosolar nebula. The results show that pure CO molecules are adsorbed in clathrate at fugacities twenty times lower than those of pure N_2. In the case of equimolar mixtures, CO is much preferentially adsorbed in clathrate. These computations imply that, at nebular conditions, CO has a much higher propensity than N_2 to be trapped in clathrates. Planetesimals agglomerated exclusively from clathrates in the outer part of the protosolar nebula should then be highly devoid in N_2.

1. Introduction

The important deficiency of clathrate equilibrium data at low temperatures implies the use of theoretical approaches to characterize the clathrates that could exist in conditions consistent with those encountered in planetary environments. However, the usual thermodynamic approaches such as the usual van der Waals & Platteeuw method are based on simplified intermolecular potentials calibrated on equilibrium measurements performed at higher temperatures. As a consequence, the capabilities of these simple potentials for predicting the composition of clathrates in the outer Solar System could be questionable.

Here we use grand canonical Monte Carlo simulations based on more sophisticated interatomic potentials to investigate the trapping in clathrate of a gas mixture made of CO and N_2 at thermodynamic conditions (gas temperature of 50K and pressure ranging between 10^{-11} and 4.10^{-3} Pa) covering those met in the protosolar nebula when this crystalline structure forms. To do so, we directly compute the absorption isotherms of CO, N_2 and their equimolar mixture in the case of structure I clathrate. Despite the fact that these two molecules are among the most important species taking part to the composition of the outer solar system, the number of data regarding the equilibrium compositions of their clathrates is scarce, if non-existant.

2. Modeling approach

Monte-carlo simulations in the Gibbs ensemble [1] have been performed for fugacities ranging from 10^{-11} to 4.10^{-3} Pa at a fixed temperature of 50K. Eight unit cells (2*2*2) of clathrate hydrate of cubic structure I (SI) have been simulated. The molecules of water were modeled using the well-known TIP4P/2005 model [2] and were allowed to translate and rotate during the simulation. Models for N_2 and CO molecules were taken from the literature, respectively from Potoff et al. [4] and Piper et al. [3]. The dimension of the cubic simulation box was fixed during the simulation and equal 24.06 Å. 10 millions MC steps were done including insertion, delation, translation and rotation of the molecules. For mixtures the fugacities of the two components were identical, taken into account that they are much lower than 1 Pa, the fugacity equals the partial pressure which implies that we simulated equimolar gases.

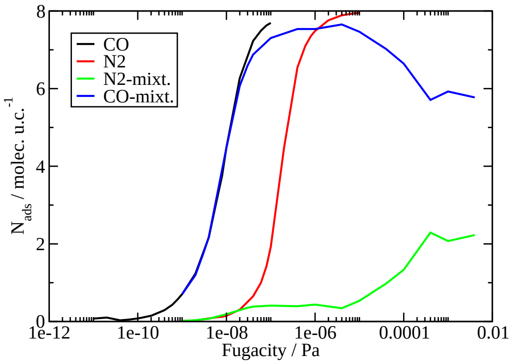

Figure 1: Isotherms of N_2, CO and their equimolar mixtures plotted as a function of the fugacity of each compound.

3. Results

Isotherms of N_2, CO and their equimolar mixtures were plotted on Fig. 1. Pure CO adsorbs at much lower fugacity than N_2, the CO isotherm reaches saturation below 10^{-7} Pa where N_2 isotherm just starts to take off. The shape are similar with a shift of 1 order of magnitude (around 20 times) in fugacity between the two species. Saturation is obtained for 8 molecules per unit cell (i.e., 1 molecule per cage). In the mixture case, the clathrate adsorbs preferentially CO. Until 2×10^{-8} Pa the CO curves of both the pure system and mixture are just on top of each others. The deviation appears when N_2 starts to be adsorbed. Nevertheless the amount of CO increases until a maximum at 4×10^{-6} Pa , under these conditions the amount N_2 is smaller than 1 molecule per unit cell. For higher fugacities a part of the CO molecules are replaced by N_2 until we observe a plateau above 4×10^{-4} Pa. At this point there are 2 N_2 for 4 CO.

4. Summary and Conclusions

Isotherms of N_2, CO and their equimolar mixtures have been computed in the Gibbs ensemble using Monte-Carlo simulations. CO is adsorbed in clathrate at lower fugacities than N_2 for pure compounds. For equimolar mixtures, CO is much preferentially adsorbed irrespective of its considered fugacity. However, mixtures with larger mole fractions of N_2 could ease the adsorption of this molecule in clathrate compared to the equimolar case. From these results, we infer that clathrates formed in the protosolar nebula and agglomerated by comets should be devoid in N_2. This mechanism does not preclude the possible incorporation of N_2 as pure ice in comets. In addition, the preferential incorporation of CO in clathrate could be consistent with the observations of the N_2-rich surfaces of Pluto and Triton. Indeed, CO could have been trapped in clathrate at higher temperature than those required for its condensation during the cooling of these bodies after their formation. In this case, CO would remain trapped in the subsurfaces of Pluto and Triton.

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References

[1] Frenkel, D. and Smit, B.: Understanding molecular simulation, Academic Press, 2002.

[2] Abascal, J. L. F. and Vega., C.: A general purpose model for the condensed phases of water: TIP4P/2005. J. Chem. Phys. vol. 123, 234505, 2005.

[3] Piper, J., Morrison, J. A. and Peters, C.: The adsorption of carbon monoxide on graphite. Mol. Phys. vol. 53, 1463, 1984.

[4] Potoff, J.J and Siepmann, I.: Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. AICHE J. vol 47, 1676, 2001.