

氏名	LUKMAN HAKIM
授与した学位	博士
専攻分野の名称	理学
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学位授与の要件	自然科学研究科 機能分子化学専攻 (学位規則第5条第1項該当)
学位論文の題目	Study on structure and thermodynamic stability of water, aqueous solution, and ice (水, 水溶液, 氷の熱力学的安定性および構造に関する研究)
論文審査委員	教授 田中 秀樹 教授 甲賀研一郎 教授 石田 祐之

学位論文内容の要旨

The search for practical hydrogen storage materials to meet the demand on environmentally clean and efficient fuel leads to the intensive exploration of hydrogen storage in supermolecular compounds consisting of simple molecule. The synthesis of the hydrogen clathrate of classical structure II implies that hydrogen molecules, despite of their small size as guest species, can stabilize a variety of host lattices of water. It was also reported that hydrogen molecules can be engaged in the interstitial spaces of ice II and ice Ic. Given the variety of hydrogen hydrates, it is of fundamental importance that the phase behavior of a water-hydrogen system be systematically studied in the P, T, and chemical-composition space. A hybrid Grand-canonical Monte Carlo simulation has been carried out to investigate the accommodation of hydrogen molecules inside ice II (C_1) and ice Ic (C_2). It is found that the existence of hydrogen molecules enhances the stability of ice II and ice Ic structures, and thus shifts their phase boundary to higher pressure and temperature. The molar ratio of hydrogen-water in both compounds is perfectly reproduced by the simulation. It is also observed that C_2 structure is degraded to amorphous under high pressure when the molar ratio of hydrogen-water fall bellows certain value depending on temperature. We also propose a theoretical approach, based on extension of van der Waals Platteeuw theory, combined with MC simulation to calculate the occupancy of hydrogen, which serve to account for the stability of C_1 and C_2 compound. The estimated hydrogen occupancy inside ice Ic agrees well with that from the simulation in high occupancy region but deviates significantly in low occupancy because the theoretical calculation has no information on the stability of the host structure in the absence of hydrogen at any pressures. This situation, however, is match with the case of C_1 , hence similar method is applied to C_1 by dividing each cylindrical-channel into cells, each of which contains only a single guest molecule. The obtained result agrees well with the MC simulation over the entire pressure and temperature range studied. The successful predictions by this theoretical calculation indicate that an underlying mechanism in the accommodation of hydrogen is simple: It is determined by the free energy of cage occupation which is in turn dominated by the vacant space for a hydrogen molecule to be engaged. The chemical potential of both ice structures are calculated from the water-hydrogen stoichiometries of both ices to explain the existence of a particular structure in place of the other. The investigation leads to a novel phase diagram for hydrogen hydrates of ice II and ice Ic (cubic ice) structure in pressure, temperature, and composition plane. The obtained phase behaviors for C_1 and C_2 are in good agreement with the experimental evidence in pressure and temperature plane where C_2 substitutes C_1 at higher pressure region.

Light noble gases such as helium and neon have been generally believed to be unable to form clathrate hydrates although the prospect for light gas to occupy the cavities of ice structure was noted from the solubility of helium and neon inside ice I_h . However, Londono et al. showed the possibility of helium to be accommodated inside ice II. A novel gas hydrate of hydrogen has been reported where water lattice formed a diamond-like structure equal to cubic ice (ice Ic), termed C_2 . Despite the fact that ice Ic itself is metastable confirmed from an experiment and simulation study, the resultant hydrate is stable. This indicates that the inclusion of guest particles stabilizes the ice structures. The stability of neon hydrate compound is investigated in the terms of the chemical potential of water. It is shown that ice Ic filled neon is stable under high pressure of GPa order and high temperature, suggesting the possibility for the existence of a novel neon hydrate compound. The chemical potential of water in the compound is found to be lower than in ice II filled with neon and lower than ice VII at high pressure. This implies that, at higher pressure, ice Ic filled with neon is the most favorable structure and the transformation from ice II to ice Ic filled with neon, can be expected.

論文審査結果の要旨

A hybrid Grand-canonical Monte Carlo simulation has been carried out to investigate the accommodation of hydrogen molecules inside ice II (C_1) and ice I_c (C_2). It is found that the existence of hydrogen molecules enhances the stability of ice II and ice I_c structures, and thus shifts their phase boundary to higher pressure and temperature. The molar ratio of hydrogen-water in both compounds, obtained from experimental work, is reproduced perfectly by the simulation. A theoretical calculation, based on extension of der Waals Platteeuw theory, is devised to construct a global phase diagram of hydrogen hydrates and related ices in pressure, temperature, and composition axes for the first time. The obtained phase diagram for C_1 and C_2 are in good agreement with the experimental evidence in pressure and temperature plane where C_2 substitutes C_1 at higher pressure region.

The stability of neon hydrate compounds is investigated in the terms of the terms of the chemical potential of water. It is shown that ice I_c filled with neon is stable under pressure of GPa order and high temperature, suggesting the possibility for the existence of a novel neon hydrate compound. The chemical potential of water in the compound is found to be lower than in ice II filled with neon and lower than ice VII at high pressure. This implies that, at higher pressure, ice I_c filled with neon is the most favorable structure and the transformation from ice II to ice I_c filled with neon, can be expected.

Adsorption of metals in aqueous solution by a certain ligand attached to polymeric support may not be ruled by merely electron pair donation between metal and the ligand, since multiple interactions may occur in aqueous solution. To examine this issue, four novel chelating resins with chitosan as polymeric support were synthesized and their adsorption behavior toward metal ions was studied in various thermodynamic conditions. An automated pretreatment system was also developed to assist the application of resin in metal collection and quantification.

The above research works have been published or accepted or publication in prestigious journals such as Physical Review Letters. Thus, the applicant deserves PhD.