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# Synthesis of carbon dioxide hydrate using lithium chloride solution and its thermochemical properties

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**The experimental device to prepare gas hydrate.**

The reactor is stainless steel cylinder (⌀ 48 mm, h = 80 mm, Pmax = 10 MPa). The lid was equipped with valves for gas supply/discharge and hermetically sealed by sealing rings. Gas phase parameters were recorded by OWEN PD100-DI10.0-111-0.5 (±0.5%) pressure sensor and OWEN DTS054-50B.V3.50 (±0.05 K) temperature sensor; second temperature sensor of the same type was installed at reactor basis. The signals were recorded with a frequency of 1 Hz (MasterSCADA). The temperature regime was provided by FT-205-25 ("LOIP") liquid cryostat with –1.5 K antifreeze (flow rate 10.5 l/min, stability ±0.2 K). $CO_2$ (purity > 99.995%) was supplied from 40-liter balloon through reducer.

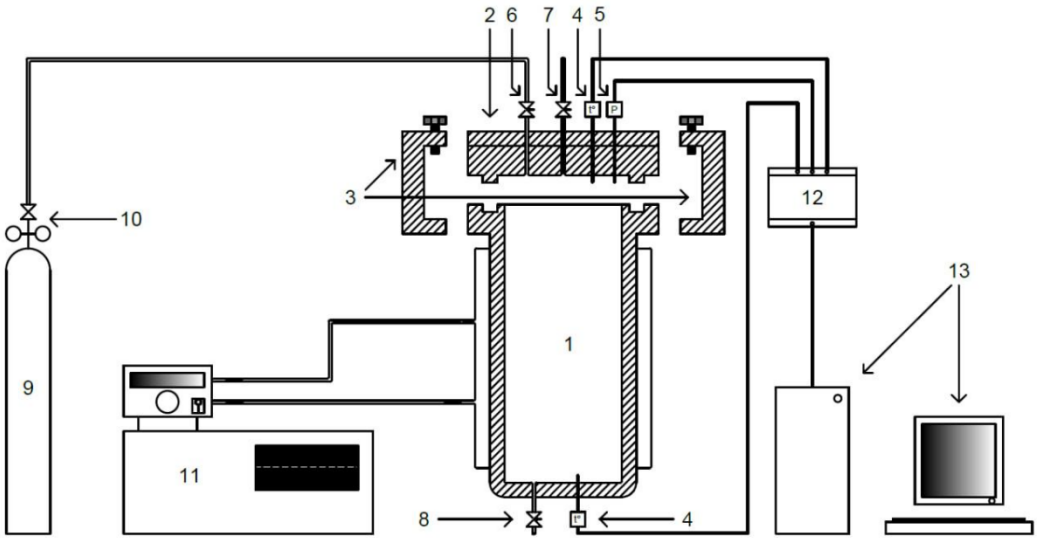


**Figure S1** Schematic diagram of experimental device: 1 – autoclave; 2 – sealed lid; 3 – sealing rings; 4 – temperature sensors; 5 – pressure sensor; 6 – gas inlet valve; 7 – gas discharge valve; 8 – bottom valve; 9 – $CO_2$ balloon; 10 – reducer; 11 – cryostat; 12 – ADC (Analog-to-digital converter); 13 – PC (personal computer).

1% lithium chloride solution was prepared from distilled water, lithium carbonate, and hydrochloric acid. The required amount of lithium carbonate (>99.9% purity) was placed in volumetric flask, and calculated amount of hydrochloric acid (2 M HCl) was added until carbon dioxide no longer bubbled and lithium carbonate was dissolved. Distilled water was then added to flask to reach desired volume.

The carbon dioxide content in obtained gas hydrate was determined by weight method. The hydrate was placed in weighed Teflon cuvette and weighed. The weight of hydrate was determined by difference between cuvette with hydrate and empty cuvette. The cuvette was left for 7 days to allow the carbon dioxide to leave hydrate. After that, the cuvette was weighed again and amount of carbon dioxide that had left was determined.

**Method of molecular dynamics modeling.**

To accurately determine the thermodynamic properties of clathrate hydrates and phase equilibrium, our theoretical group developed a methodological approach based on the van der Waals–Platteeuw (vdW-P) theory of solid solutions, incorporating several modifications. These

improvements account for host-lattice relaxation, guest–guest interactions, and the quantum nature of guest vibrational states in the hydrate matrix.

The phase equilibrium line was constructed by numerically determining the chemical potentials of water molecules forming the hydrate lattice and guest molecules located in different types of cages. The equilibrium composition of the hydrate phases was obtained from the condition of equality between the chemical potentials of guest molecules in the hydrate phase and in the gas (or liquid) phase.

Pure $CO_2$ hydrate crystallizes in the structure type sI, which contains 2 small $5^{12}$ (S) cages, 6 large $5^{12}6^2$ (L) cages, and 46 $H_2O$ molecules per unit cell. $CO_2$ molecules can occupy both the large and small cages. In this study, structure sII hydrates with single occupancy of both L and S cages were also considered. Ice Ih was modeled using a supercell consisting of 32 unit cells (128 $H_2O$ molecules).

Coulombic interactions were calculated using the Ewald summation method, with hydrogen atom positions satisfying the "ice rule" and ensuring zero net dipole moment for all simulated structures. Proton ordering was set according to the Bernal–Fowler rules, and the orientation of water molecules was adjusted to yield a total dipole moment not exceeding 0.1% of the dipole moment of a single $H_2O$ molecule.

Water–water interactions were described using the modified SPC/E potential with Lennard–Jones parameters $\sigma = 3.1556$ Å and $\varepsilon = 0.65063$ kJ/mol; the hydrogen and oxygen charges were $q_H = +0.4238|e|$ and $q_O = -0.8476|e|$, respectively.

Guest–guest and guest–water interactions were modeled using the Lennard–Jones potential with parameters $\sigma = 4.000$ Å and $\varepsilon = 1.5798$ kJ/mol for $CO_2$, and $\sigma = 1.409$ Å and $\varepsilon = 1.409$ kJ/mol for $Li^+$ ions. In addition, for the chloride ion ($Cl^-$) compatible with SPC/E water, we used Lennard–Jones parameters $\sigma = 0.43$ nm (4.30 Å) and $\varepsilon = 0.42$ kJ/mol, optimized against pair solvation free energies and activity coefficients with standard Lorentz–Berthelot mixing rules.